Separated quadrupolar field experiment

Rajeev Kumar, Wen Ling, Wolfgang Schoefberger, Alexej Jerschow*

Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, USA

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Abstract

We describe an NMR experiment that produces spectra correlating the first-order quadrupolar spectrum and the central transition spectrum of half-integer quadrupolar spins, allowing one to separate the quadrupolar parameters in overlapping spectra under both static and magic-angle-spinning conditions. Promising fields of applications include situations where the sample cannot easily be rotated, or where it cannot be rotated at the magic angle.
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1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy of nuclei with spins larger than 1/2 has become a very useful and important technique for the structural characterization of materials including glasses, ceramics, catalysts, and semiconductors. These nuclei are subject to quadrupolar coupling which often dominates other NMR-active interactions in the system [1]. Extracting information about the quadrupolar interaction from solid-state NMR spectra can give important insights into the structural and dynamical aspects of solids, as it is a sensitive reporter of the electrostatic potential surrounding an atom. Jakobsen and others [2,3] have used the intensities of the spinning sidebands in magic-angle spinning (MAS) experiments to determine quadrupolar coupling constants and asymmetry parameters with good precision. Under relatively rapid spinning conditions, the sideband manifolds of individual sites may be separated. When the spinning speed is small, under off-magic-angle spinning, or under static conditions, however, this is no longer possible. The problem is particularly acute for spins larger than 3/2 in which case additional satellite transition manifolds occur. We report here a method that allows one to correlate the first-order quadrupolar spectrum with the central transition in a two-dimensional experiment. While this method does not allow the removal of the second-order broadening, it is applicable to the static case, the slow MAS, and the off-MAS cases. This complements existing high-resolution experiments such as DAS [4–6], DOR [7,8], MQMAS [9,10], and STMAS [11], which may not reveal their full power in the static and slow-spinning regimes.

We expect that the demonstrated technique will be useful for structure and dynamics investigations in solids that are either not amenable to rapid sample spinning (such as in the case of ex situ NMR [12,13] or surface-coil NMR), where off-magic-angle spinning is desired, or where information complementary to second-order interactions is sought. Based on the similarity of the appearances of the spectra with those obtained from separated-local-field experiments (SLF) [14], we wish to call it static or slow-MAS separated quadrupolar field (SQF) experiment.

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* Corresponding author.
E-mail address: alexej.jerschow@nyu.edu (A. Jerschow).

2. Results and discussion

The central transition of half-integer quadrupolar nuclei (the transition between the states $m = +1/2$ and $m = -1/2$) is the easiest transition to be detected directly as it is unaffected by the first-order quadrupolar interaction and we shall be interested in cases where the appearance of the second-order effect is unimportant or cannot be avoided (such as in the case of relatively large magnetic fields [15], or in static experiments). In many cases, the resolution thus provided is sufficient to distinguish between inequivalent sites in a solid. Satellite transitions, on the other hand, have broad spectroscopic features in a powder sample, since the strength of the quadrupolar interaction depends on orientation. In order to obtain a correlation spectrum that encodes the first-order quadrupolar interaction in one dimension and the narrow spectroscopic features in another, one therefore needs to excite the satellite transitions to produce frequency labeling in t_1 and subsequently use a coherence transfer into the central transition for direct detection during t_2. The experiment that we introduce is shown in Fig. 1.

After the application of a short and strong RF pulse the magnetization of the satellite transitions evolves under the action of the first-order quadrupolar interaction. The coherence transfer between the satellite and the central transition is performed by a double-frequency sweep (DFS) [16,17]. We experienced that this operation was more reliable when this sweep was flanked by short and strong RF pulses (as represented in Fig. 1). In such a case the DFS operates on the diagonal components of the density matrix and phase errors are largely avoided. Broadband excitation is insured by using relatively short pulses. Delays before and after the DFS, in addition to proper phase cycling, can help to minimize artifacts by allowing unwanted magnetization components to dephase. The DFS is designed for inverting the satellite transitions, but in practice partially saturates them, in particular, in spinning samples, as shown in Fig. 2. Here, we illustrate the suppression of sidebands in a mixture of $NaNO_3$ with $NaClO_3$. For the two-dimensional correla-
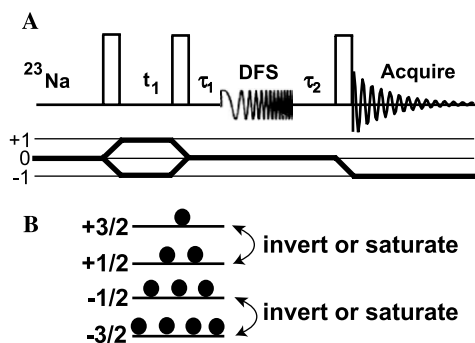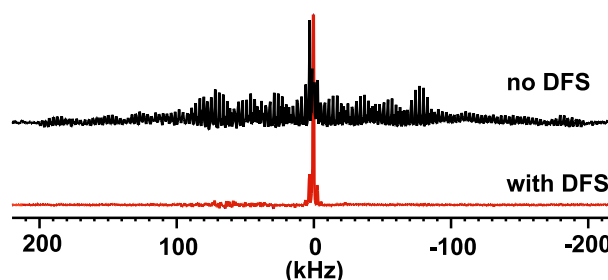

Fig. 2. ^{23}Na MAS spectra of $NaNO_3$ + $NaClO_3$ at a spin rate of 3 kHz showing the spinning sidebands and the central transition. (Top) Simple one-pulse experiment. (Bottom) One-pulse experiment after the application of a DFS showing the suppression of spinning sidebands.

tion experiment, the saturation of the satellite transitions is quite a favorable process as it minimizes the appearance of the satellite transitions in the directly observed dimension (F2), where one wishes to display the central transition components only. In the SQF experiment the DFS serves to perform a coherence transfer between the satellite transitions and the central transition. The result is a two-dimensional spectrum that displays the first-order quadrupolar spectrum along F1 and the central transition spectrum in F2.

Fig. 3 shows the static ^{23}Na SQF spectra taken of a powdered mixture of $NaNO_3$ and $NaClO_3$, as well as, the slices through the two-dimensional spectra for the two components. It displays the broadening resulting from the first-order quadrupolar coupling in one dimension and narrow peaks in the other. The F2 dimension shows the central transition peaks and may display additional broadening due to the second-order quadrupolar coupling and, in the static case, due to chemical-shift anisotropy (CSA), as well as, dipolar couplings. In Fig. 3 the central transition signals are observed as negative peaks. This is a result of the partial inversion of the satellite transitions in the course of the coherence transfer (the satellite transition signals are displayed as positive peaks in the spectrum). Also, in F1 there is a zero-frequency artifact, which arises from the fact that the coherence transfer from the satellite transitions to the central transitions is not perfect. One may be able to remove these artifacts by the use of a double-quantum filter [18]. They do not, however, affect the quality of the slices. Importantly, there is no artifact arising from a satellite-to-satellite transition coherence transfer, which would appear as a diagonal or an anti-diagonal. Such artifacts would be more harmful to the appearance of the spectra. There is a slight asymmetry in the extracted slices, which presumably arises from small phase errors.

The static SQF spectrum shows that the first-order lineshapes are very close to the theoretical ones, except that the central transitions are inverted (as discussed above). The simulated spectra were calculated using the values found independently in one-dimensional experiments of the individual components and in
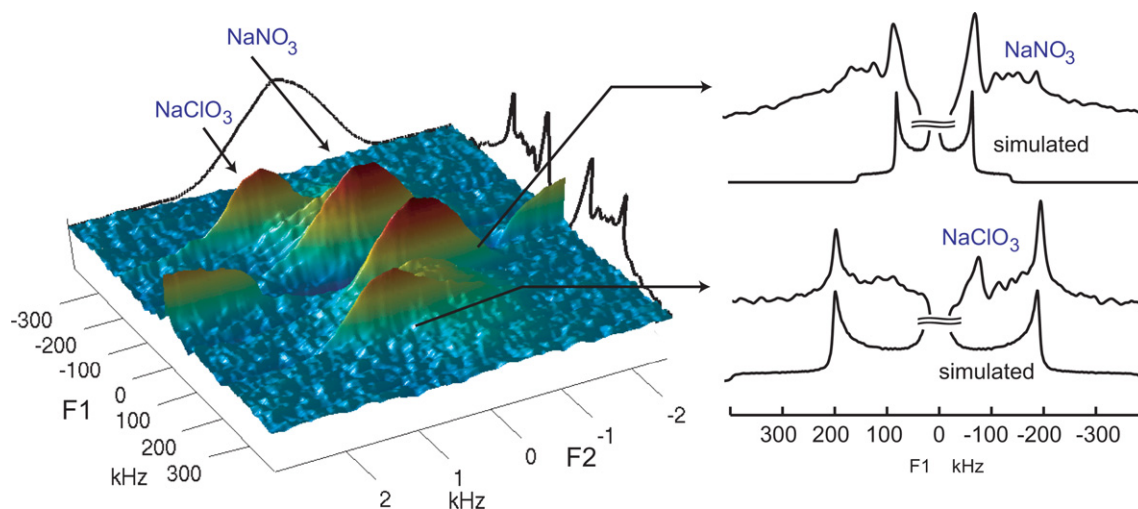

Fig. 1. (A) SQF pulse sequence. (B) Energy level diagram illustrating the function of the DFS for saturation or inversion.

Fig. 3. Static SQF spectrum of a 50:50% mixture of $NaNO_3$ and $NaClO_3$. Slices through the two-dimensional data were taken for the two components and are compared to simulated quadrupolar lineshapes.
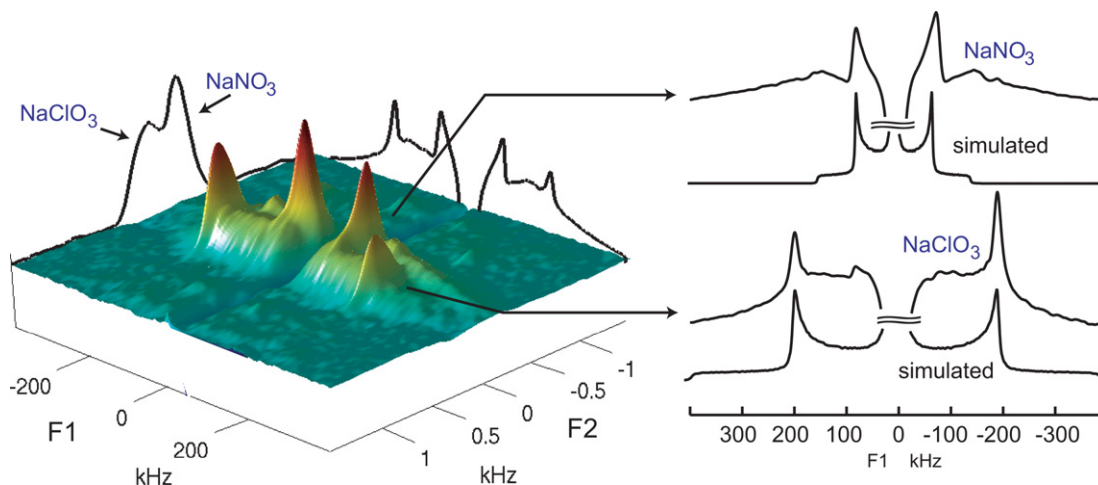

Fig. 4. One kHz MAS SQF spectrum of a 50:50% mixture of $NaNO_3$ and $NaClO_3$. Slices through the two-dimensional data were taken for the two components and are compared to theoretical lineshapes.

MQMAS experiments ($C_q = 0.32$ MHz, $\eta = 0.0$ for $NaNO_3$ and $C_q = 0.79$ MHz, $\eta = 0.0$ for $NaClO_3$). The separation between the slices in the SQF experiment may be even better at a higher magnetic field.

The 1 kHz MAS SQF spectrum of the same mixture is shown in Fig. 4. The separation of the two components is now significantly better than in the static experiment as a result of the partial removal of second-rank interactions. Some distortions are visible in the slice for $NaNO_3$. These are due to the fact that the DFS pulse is not very fast compared to the rotor period. Nevertheless, qualitative agreement between the slices and the theoretical (static) lineshapes is reasonably good. We experimented with various durations of the DFS, including very short and rotor-synchronized ones and we did not see any improvements in the lineshapes or signal

intensities. Very short DFS pulses are limited by the spectrometer time resolution, which then leads to non-ideal pulse shapes. In such a case the signals of both the central and satellite transitions are significantly perturbed. We expect that by using frequency modulators external to the spectrometer to create the DFS pulse [16,17], one may achieve superior results. Other approaches for performing the coherence transfer were tested, such as fast amplitude modulation (FAM) [19], and rotor assisted population transfer (RAPT) [20], but yielded distorted lineshapes. We believe that these methods are more appropriately used at larger spinning speeds. Under static conditions FAM methods produced lineshapes with an overemphasis of the regions located at the modulation frequency of the FAM pulse train.

In many ways the SQF experiment provides information similar to nutation experiments [21], namely the association of central transition peaks with quadrupolar parameters. The two appear to be complementary in their power and scope. SQF, for example, is less prone to B_1 inhomogeneities and has the prospect of providing better η values. The nutation experiment, on the other hand, may perform more reliably for larger quadrupole coupling constants.

Several variants of this experiment are currently being investigated. It may be favorable to interchange the frequency labeling periods, such that the central transition spectrum would be along F1 and the first-order quadrupolar spectrum along F2. This could be achieved by first saturating the satellite transitions, frequency labeling during t_1 based on the frequencies of the central transition, then transferring the coherence to the satellite transitions and detection during t_2. Initial tests showed, however, that the transfer from the central transition to the satellite transitions is not as reliable as the opposite transfer. Some modification of the DFS may be in order in such a situation. We are also investigating the extension of the applicability of this method to nuclei with spins larger than 3/2. An inward-sweeping DFS [17] appears to be most useful in such a situation.

One may likewise view the SQF experiment as a variant of STMAS under slow spinning or static conditions. Indeed, it is conceivable to perform very slow spinning STMAS with the t_1 increment covering small fractions of the rotor period. Spinning sidebands will then appear in F1, which produce a first-order-like spectrum in F1. An additional advantage of that experiment would then be that one could obtain a correlation spectrum of the first-order, the second-order and the isotropic spectrum at the same time via a shearing transformation of individual spinning sideband manifolds. This experiment, however, would require pristine spectral resolution in F1. We did not succeed in performing this experiment, likely as a result of spinning angle and speed instabilities.

3. Experimental parameters

The experiment is demonstrated for ^{23}Na NMR of a powdered solid mixture of $NaNO_3$ with $NaClO_3$ (50:50%). The compounds were purchased from Aldrich and used without further purification. The experiments were performed on a Bruker Avance 400 MHz spectrometer operating at a ^{23}Na Larmor frequency of 105.8 MHz. A 4 mm MAS rotor was used on a double-resonance CPMAS probe and the mixture was center-packed. The RF powers used for the excitation and conversion were 62.5 kHz. The pulse durations were 1.5 μs and the recycle delay was 1 s. The coherence transfer from the satellite to the central transitions was achieved using a 300 μs long DFS consisting of 1000 points with a linear modulation frequency sweep from 20 to 550 kHz using an RF power of 22.1 kHz. Spectral windows of $1000 \text{ kHz} \times 20 \text{ kHz}$ were covered in the experiments of Figs. 3 and 4 with the acquisition of 256 t_1 and 1024 t_2 data points. The number of transients for each t_1 increment was 256. The MAS speed was 1 kHz for the experiment of Fig. 4. All the pulses including the DFS in the SQF experiment were phase cycled independently by 0° and 180°, and pure-phase lineshapes were obtained using the States-TPPI method.

4. Conclusion

This novel method produces spectra correlating the first-order quadrupolar spectrum of the satellite transitions with the central transition spectrum of half-integer quadrupolar spins, allowing one to separate the sub-spectra of inequivalent sites under both static and MAS conditions. Near-theoretical first-order lineshapes are obtained under static conditions, and slightly distorted lineshapes under spinning conditions due to the interference of spinning with the satellite-to-central transition coherence transfer. We expect that an improved coherence transfer procedure can be found to correct for this. The second-order broadenings become smaller and the peak separations larger at higher magnetic fields and this method may therefore become especially useful at elevated magnetic fields. Even in the presence of CSA effects static experiments of this kind can allow for a distinction between different components in the sample. Promising areas of applications include situations where the sample cannot easily be rotated, or where it cannot be rotated at the magic angle. Another field of application of these types of experiments is the separation of CSA and quadrupolar sidebands, which we are currently investigating. We are also evaluating this method with respect to more efficient coherence transfers, the robustness against artifacts, and the extension to larger quadrupole coupling constants. Finally, we would like to point out that the DFS-type coherence transfer employed here may also be useful for improving the sensitivity of STMAS [11] experiments.

References

[1] D.D. Laws, H.-M.L. Bitter, A. Jerschow, Solid-state NMR spectroscopic methods in chemistry, Angew. Chem. Int. Ed. Engl. 41 (2002) 3096–3129.

[2] M.R. Hansen, T. Vosegaard, H.J. Jakobsen, J. Skibsted, B-11 chemical shift anisotropies in borates from B-11 MAS, MQMAS, and single-crystal NMR spectroscopy, J. Phys. Chem. A 108 (2004) 586–594.

[3] J. Skibsted, H.J. Jakobsen, ^{35}Cl and ^{37}Cl magic-angle spinning NMR spectroscopy in the characterization of inorganic perchlorates, Inorg. Chem. 38 (1999) 1806–1813.

[4] A. Llor, J. Virlet, Towards high-resolution NMR of more nuclei in solids: sample spinning with time-dependent spinner axis angle, Chem. Phys. Lett. 152 (1988) 248–253.

[5] K.T. Mueller, B.Q. Sun, G.C. Chingas, J.W. Zwanziger, T. Terao, A. Pines, Dynamic-angle spinning of quadrupolar nuclei, J. Magn. Reson. 86 (1990) 470–487.

[6] I. Farnan, P.J. Grandinetti, J.H. Baltisberger, J.F. Stebbins, U. Werner, M.A. Eastman, A. Pines, Quantification of the disorder in network-modified silicate glasses, Nature 358 (1992) 31–35.

[7] A. Samoson, E. Lippmaa, A. Pines, High-resolution solid-state NMR. Averaging of second-order effects by means of a double-rotor, Mol. Phys. 65 (1988) 1013–1018.

[8] B.F. Chmelka, K.T. Mueller, A. Pines, J. Stebbins, Y. Wu, J.W. Zwanziger, Oxygen-17 NMR in solids by dynamic-angle spinning and double rotation, Nature 339 (1989) 42–43.

[9] L. Frydman, J.S. Harwood, Isotropic spectra of half-integer quadrupolar spins from bidimensional magic-angle spinning NMR, J. Am. Chem. Soc. 117 (1995) 5367–5368.

[10] A. Medek, J.S. Harwood, L. Frydman, Multiple-quantum magic-angle spinning NMR: a new method for the study of quadrupolar nuclei in solids, J. Am. Chem. Soc. 117 (1995) 12779–12787.

[11] Z. Gan, Isotropic NMR spectra of half-integer quadrupolar nuclei using satellite transitions and magic-angle spinning, J. Am. Chem. Soc. 122 (2000) 3242–3243.

[12] C.A. Meriles, D. Sakellariou, H. Heise, A.J. Moule, A. Pines, Approach to high-resolution ex situ NMR spectroscopy, Science 293 (2001) 82–85.

[13] C.A. Meriles, D. Sakellariou, A. Moule, M. Goldman, T.F. Budinger, A. Pines, High-resolution NMR of static samples by rotation of the magnetic field, J. Magn. Reson. Ser. A 169 (2004) 13–18.

[14] R.K. Hester, J.L. Ackerman, B.L. Neff, J.S. Waugh, Separated local field spectra in NMR: determination of structure in solids, Phys. Rev. Lett. 36 (1976) 1081–1083.

[15] P.J.M. van Bentum, J.C. Maan, J.W.M. van Os, A.P.M. Kentgens, Strategies for solid-state NMR in high-field Bitter and hybrid magnets, Chem. Phys. Lett. 376 (2003) 338–345.

[16] D. Iuga, H. Schafer, R. Verhagen, A.P.M. Kentgens, Population and coherence transfer induced by double frequency sweeps in half-integer quadrupolar spin systems, J. Magn. Reson. 147 (2000) 192–209.

[17] D. Iuga, A.P.M. Kentgens, Influencing the satellite transitions of half-integer quadrupolar nuclei for the enhancement of magic angle spinning spectra, J. Magn. Reson. 158 (2002) 65–72.

[18] H.T. Kwak, Z.H. Gan, Double-quantum filtered STMAS, J. Magn. Reson. 164 (2003) 369–372.

[19] T. Brauniger, K. Ramaswamy, P.K. Madhu, Enhancement of the central-transition signal in static and magic-angle-spinning NMR of quadrupolar nuclei by frequency-swept fast amplitude-modulated pulses, Chem. Phys. Lett. 383 (2004) 403–410.

[20] H.T. Kwak, S. Prasad, T. Clark, P.J. Grandinetti, Selective suppression and excitation of solid-state NMR resonances based on quadrupole coupling constants, J. Magn. Reson. 160 (2003) 107–113.

[21] A.P.M. Kentgens, Off-resonance nutation NMR spectroscopy of half-integer quadrupolar nuclei, Progr. Nucl. Magn. Reson. Spectrosc. 32 (1998) 141–164.