

Distribution effects on ^1H double-quantum MAS NMR spectra

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Abstract

The effect of a distribution in the ^1H – ^1H dipolar coupling on ^1H double-quantum (DQ) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spinning sideband patterns is considered. In disordered or amorphous materials a distribution in the magnitude of the ^1H – ^1H dipolar coupling is a realistic possibility. Simulations of the ^1H DQ MAS NMR spinning sideband spectra were performed with the two-spin approximation. These simulations reveal that a dipolar coupling distribution can greatly affect the DQ spectral shape and behavior of the DQ build-up. The spectral line shapes are quantified by measurement of the relative intensities of the DQ sidebands. These variations in the ^1H DQ NMR spectra are evaluated as a function of the width of the dipolar coupling distribution. As an example, the experimental DQ spinning sideband spectrum for a hydrated polyoxoniobate containing 15 H_2O molecules per hexaniobate cluster, are better simulated with a distribution of dipolar couplings opposed to a single coupling constant.

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1. Introduction

The development of high-speed ($\nu_R > 25$ kHz) magic angle spinning (MAS) probes allows improved resolution in the ^1H NMR spectrum of rigid solids by averaging the homonuclear dipolar coupling [1,2]. Rotor-synchronized multiple-pulse sequences like back-to-back (BABA) [3,4], CN-type sequences [5], and dipolar restoration at the magic angle (DRAMA) [6], can be exploited to reintroduce the dipolar coupling averaged by MAS in order to indirectly observe the double-quantum (DQ) coherences between pairs of protons in a two-dimensional (2D) fashion. Such 2D ^1H correlation experiments have been successfully employed in the structural and dynamic investigations of hydrogen-bonded [7–9], dendritic [10], liquid crystalline (LC) [11], and polymeric materials [12–16]. In rigid systems the highly resolved single-quantum (SQ) ^1H MAS spectrum yields the rich chemical information via the chemical shift while the ^1H – ^1H dipolar coupling and the corresponding distance can be extracted from the DQ side-

band manifold through spectral simulations [17]. In mobile systems the ^1H – ^1H dipolar interaction is averaged and the magnitude of the extracted coupling constant from the DQ spectrum can yield characteristic information regarding the motional averaging process [11,14].

A distribution of dipolar couplings is expected to occur in dynamically averaged solids where a single chemical environment can have a range of molecular motions. Distribution effects have been well documented on heteronuclear NMR experiments like rotational-echo double resonance REDOR [18], and homonuclear dephasing techniques like DRAMA, controlled simple excitation for dephasing rotational amplitudes (CEDRA), and Dante-Selective REDOR (DSR) experiments [19]. There has also been some focus on the impact of a dipolar coupling distribution in the context of ^1H multiple-quantum (MQ) spin-counting experiments [20,21]. However, there have been very few studies directed toward the effect of distributions on ^1H DQ MAS NMR spinning sideband patterns [11,22]. Brown and co-workers demonstrated that for a series of LC compounds a distribution of dipolar couplings existed due to a range of motional order parameters [11].

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The distribution in the motional order parameters was the result of different orientations of the CH₂H–H vector with respect to the rotational axis of the LC phase [11]. While that work provided a single example of the influence of distributions, a more thorough investigation of dipolar coupling distribution effects on ¹H DQ sideband patterns has yet to be reported. If the analysis of ¹H DQ sidebands is to be extended to amorphous and disordered systems, where variability in ¹H–¹H distances and mobility are expected, the impact dipolar coupling distributions have on the DQ spinning sideband patterns needs to be evaluated.

The focus of the present communication is to analyze the effect a distribution in ¹H homonuclear dipolar coupling has on the DQ spinning sideband patterns and build-up curves. Spectral simulations into the effect of distributions on the DQ spinning sideband pattern and DQ intensity build-up will be presented. Simulations of the DQ ¹H sidebands from an experimental example involving a hydrated polyoxoniobate material are presented to demonstrate the influence of a distribution on the observed spectra.

2. Simulations

The theory of multiple-quantum coherences in MAS NMR at high spinning speeds is well developed [22–24]. The DQ time-domain signal (S_{DQ}) for an isolated spin-1/2 pair using the BABA recoupling pulse sequence to generate DQ coherences is given by [22]:

$$S_{DQ}(t_1; t_2 = 0) = (\cos 2\Delta\omega_{PC}t_1) \left\langle \sin \left[\frac{3}{\pi\sqrt{2}} D^{ij} \sin(2\beta^{ij}) \cos(\gamma^{ij}) + \omega_R t_1 N\tau_R \right] \sin \left[\frac{3}{\pi\sqrt{2}} D^{ij} \sin(2\beta^{ij}) \cos(\gamma^{ij}) N\tau_R \right] \right\rangle, \quad (1)$$

where β^{ij} and γ^{ij} are the Euler angles relating the principal axes system of the dipolar tensor to the rotor-fixed reference frame, $\langle \rangle$ indicates a powder average, τ_R is the rotor period, ν_R is the MAS spinning frequency ($\omega_R = 2\pi \times \nu_R$), $N\tau_R$ is the duration of the excitation and reconversion periods, $\Delta\omega_{PC}$ is the frequency increment for TPPI phase cycling, and D^{ij} is the dipolar coupling between spins i and j . In rigid systems the dipolar coupling is given by:

$$D^{ij} = \frac{\mu_0 \hbar \gamma_i \gamma_j}{4\pi r_{ij}^3}, \quad (2)$$

where r_{ij} is the internuclear distance between the two spins and γ_i and γ_j are the gyromagnetic ratios of the coupled nuclei. In the present simulations the DQ signal from Eq. (1) was modified to include a Gaussian distribution of dipolar couplings as follows:

$$S_{DQ}(t_1, \sigma) = \sum_l \rho_l \times \cos(2\Delta\omega_{PC}t_1) \left\langle \sin \left[\frac{3}{\pi\sqrt{2}} D_l^{ij} \sin(2\beta^{ij}) \cos(\gamma^{ij}) + \omega_R t_1 N\tau_R \right] \sin \left[\frac{3}{\pi\sqrt{2}} D_l^{ij} \sin(2\beta^{ij}) \cos(\gamma^{ij}) N\tau_R \right] \right\rangle, \quad (3)$$

where ρ_l is the probability of a given dipolar coupling D_l^{ij} . The distribution of dipolar couplings about a mean dipolar coupling value, \bar{D}^{ij} , with a standard deviation, σ , is given by:

$$\rho_l(D) = \frac{1}{\sqrt{2\pi}} \exp \left[- \left(\frac{\bar{D}^{ij} - D_l^{ij}}{2\sigma} \right)^2 \right]. \quad (4)$$

Simulations of the ¹H DQ MAS NMR sidebands were performed in MATLAB using Eqs. (3) and (4). Powder averages over the Euler angles were calculated with the Grant tiling scheme as previously described [25]. No correlations between D_l^{ij} and the Euler angles β^{ij}, γ^{ij} were assumed.

3. Experimental

Sodium hexaniobate, Na₇[HNb₆O₁₉]·15H₂O, was prepared as described elsewhere [26]. The ¹H MAS NMR experiments were carried out on a Bruker Avance 600 spectrometer equipped with a 2.5 mm MAS probe operating at a frequency of 600.1 MHz. The non-rotor-synchronized 2D DQ/SQ correlation experiment utilized the BABA excitation/reconversion sequence with 3.0 μs 90° pulses as detailed by Schnell and Spiess [23]. The sweep width was 500 kHz ($N = 2$) or 1 MHz ($N = 4$) and 60 kHz for the F_1 and F_2 dimensions, respectively. A 2 s recycle delay was implemented and 200 ($N = 2$) or 400 ($N = 4$) t_1 increments were collected. Rotor spinning frequencies (ν_R) were 33 kHz for all experiments. Phase cycling included the selection of DQ coherences and phase sensitive t_1 detection using the States-TPPI method [27]. The DQ ¹H spectra were obtained by taking slices along the F_1 dimension for the chemical shift of interest.

4. Results and discussion

The effect of a Gaussian distribution in ¹H–¹H dipolar coupling on the ¹H DQ MAS NMR spinning sideband manifold is depicted in Fig. 1. For an isolated two-spin system only the odd-order sidebands appear in the DQ spectrum. With increasing standard deviation (σ) of the dipolar coupling distribution the lower-order sidebands are emphasized. This result clearly displays the effect a distribution in dipolar couplings can have on

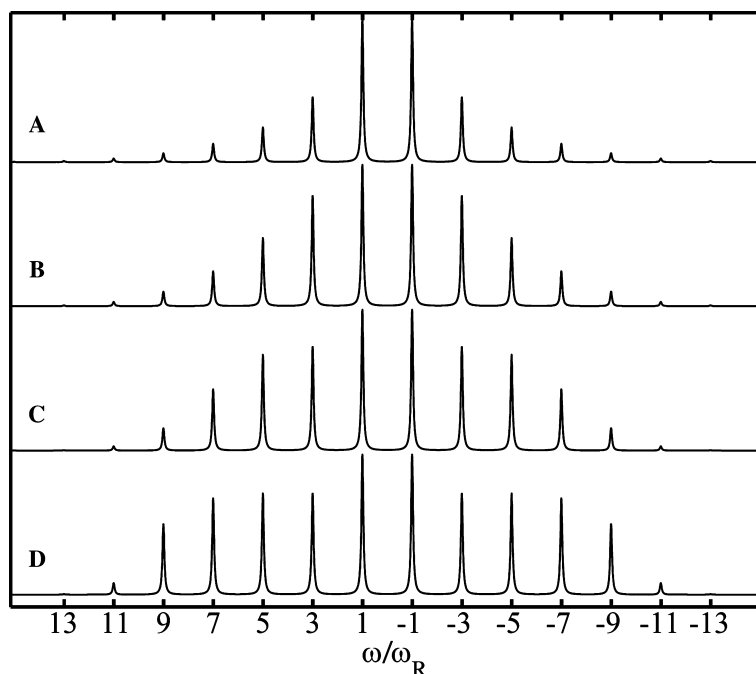


Fig. 1. Simulated ^1H DQ MAS NMR spinning sideband patterns for dipolar coupled spin-1/2 pairs under BABA excitation and reconversion with $N = 4$ and $\nu_R = 33$ kHz. The mean dipolar coupling was $\bar{D}^{ij} = 20$ kHz for differing standard deviations of the dipolar coupling distribution: (A) $\sigma = 3$ kHz (15% \bar{D}^{ij}), (B) $\sigma = 2$ kHz (10% \bar{D}^{ij}), (C) $\sigma = 1.25$ kHz (6% \bar{D}^{ij}), and (D) $\sigma = 0$ kHz.

the shape of the DQ sideband patterns particularly for large ($\sigma = 10\%$ \bar{D}^{ij} and 15% \bar{D}^{ij}) distributions. Previous ^1H DQ MAS NMR investigations have reported sideband patterns where the intensities of the lower-order sidebands (± 1 and ± 3) were inconsistent with the DQ simulations [9,14,16]. In one of these studies the simulations were fit to the higher-order sidebands ($> \pm 3$) and not the lower-order sidebands (± 1 and ± 3), due to CSA distortions of the latter [9]. It is clear from Fig. 1 that a distribution in dipolar coupling may be another factor contributing to difficulties in simulating experimental data based on differential changes of the relative sideband intensities.

The changes in the sideband intensities with distribution in ^1H DQ MAS NMR can be quantified by plotting the ratio of the odd-ordered sideband ($\pm n$) intensity to the first-order sideband (± 1) as a function of the mean dipolar coupling as shown in Fig. 2. For small distributions the sideband ratios display an oscillatory behavior similar to that observed in DQ build-up curves as a function of excitation time [22]. With increasing σ there is a damping of these oscillations (Figs. 2B–G). These sideband ratio plots can be used to extract both the average dipolar coupling and standard deviation by comparing the experimentally observed ^1H DQ sideband ratios to these simulated plots.

In the regime of small dipolar coupling (< 5 kHz), only first-order DQ spinning sidebands are typically observed, making it difficult to accurately determine the magnitude of the dipolar coupling constant from the

spinning sideband manifold. In principle the generation of higher-order sidebands is possible with small dipolar couplings by using extended excitation/reconversion times. However, in rigid proton materials the length of the excitation times necessitated to generate higher-order sidebands is limited by the reduced spin–spin relaxation times (T_2) present in highly dipolar coupled systems. For these situations the DQ intensity as a function of excitation time can be used to extract the dipolar coupling constant [22]. When a single dipolar coupling is present the DQ build-up curve displays oscillations. Again, these oscillations are damped with the introduction of a distribution in the dipolar coupling (Fig. 3). This is similar to previous observations with REDOR measurements where distributions of heteronuclear dipolar couplings damped the oscillations in the REDOR curve [18]. The DQ simulations in Fig. 3 were implemented with a 2 kHz dipolar coupling. This coupling magnitude is typical for two coupled ^{13}C spins in a rigid organic system. The oscillatory behavior in the build-up curve is observed because $\omega_R/D^{ij} \gg 1$. The ability to detect (or dismiss) dipolar coupling distributions through observation of damping (or lack of damping) in the DQ build-up curve will work for most other heteronuclear and homonuclear couplings. It should be noted that for systems with a distribution of dipolar couplings, where significant damping of the DQ oscillations is observed, the DQ build-up curves do not provide enough information for the extraction of the distribution width.

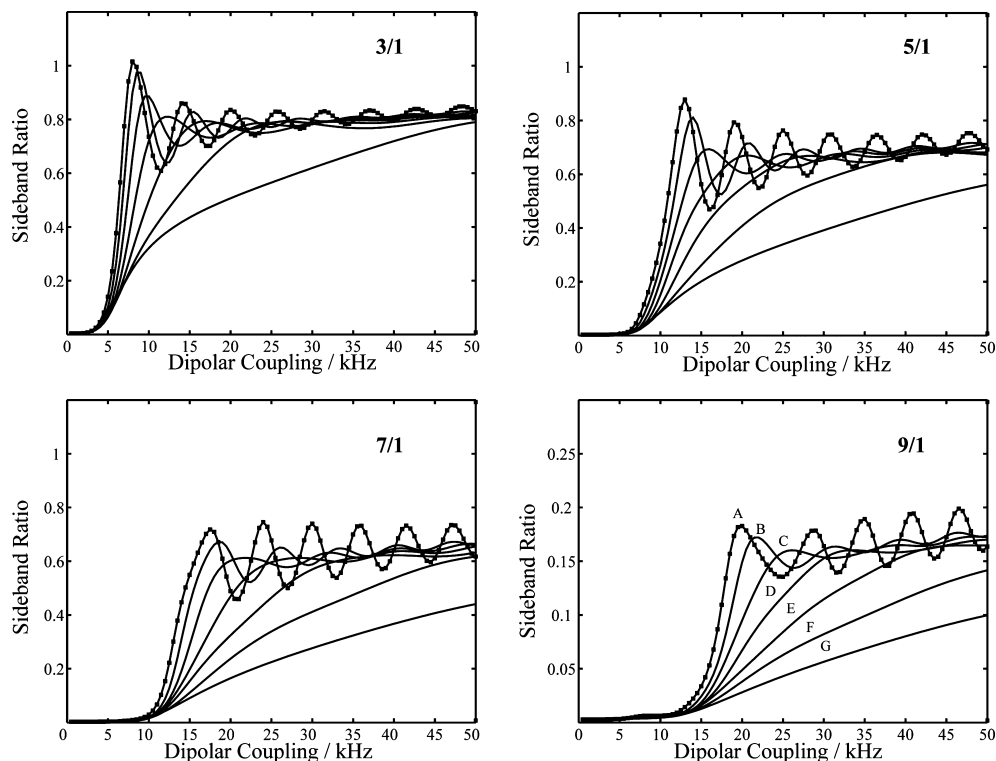


Fig. 2. Sideband ratio (ratio with respect to first-order sideband) for odd-order sidebands, as a function of \bar{D}^{ij} and σ , for $N = 4$ and $\nu_R = 33$ kHz. The sideband ratio is denoted in the figure. (A) $\sigma = 0$, (B) $\sigma = \bar{D}^{ij}/42$, (C) $\sigma = \bar{D}^{ij}/21$, (D) $\sigma = \bar{D}^{ij}/14$, (E) $\sigma = \bar{D}^{ij}/10.5$, (F) $\sigma = \bar{D}^{ij}/8.4$, and (G) $\sigma = \bar{D}^{ij}/7$.

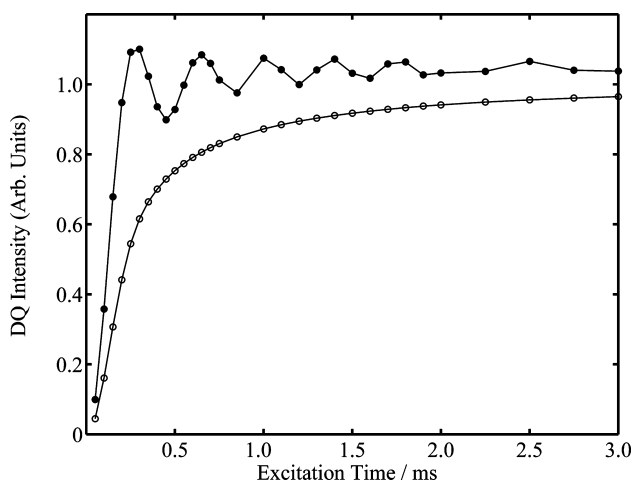


Fig. 3. Simulated ^1H DQ MAS build-up curves for dipolar coupled spin-1/2 pairs under BABA with $\nu_R = 10$ kHz. $\bar{D}^{ij} = 2$ kHz with no distribution (●) and $\sigma = \bar{D}^{ij}/6$ (○).

In the case of DQ ^1H NMR where $\omega_R/D^{ij} \approx 1$ for two isolated, dipolar-coupled, rigid protons the oscillations cannot be resolved due to the time resolution in the DQ experiment imposed by the rotor-synchronized sequences. For larger dipolar couplings (≥ 5 kHz) analysis of the DQ sidebands should be performed to determine the dipolar coupling and size of the distribution. However, in ^1H systems where there is signifi-

cant motional averaging to produce a small ^1H - ^1H effective dipolar coupling such that only first-order sidebands are observed in the DQ sideband spectrum,

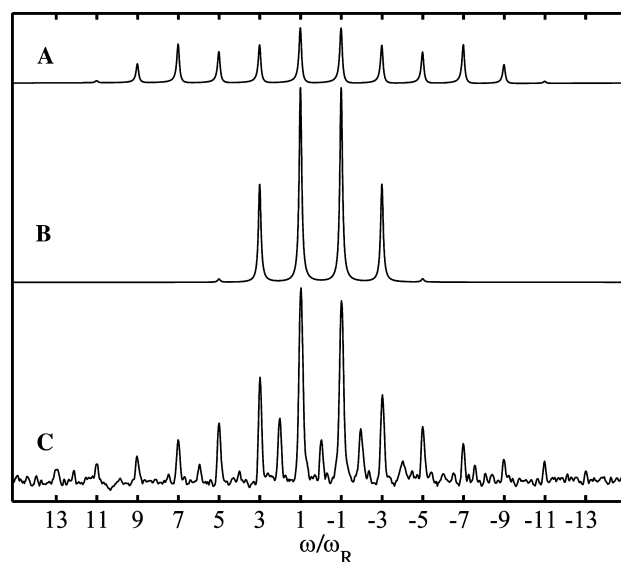


Fig. 4. ^1H DQ MAS NMR spectrum (F_1 slice taken at the water chemical shift) for sodium hexaniobate material containing 15 H_2O molecules. (A) Simulated spectrum with a single dipolar coupling equal to 19 kHz (fits ± 7 - and ± 9 -order sidebands), (B) simulated spectrum with a single dipolar coupling equal to 7 kHz (fits ± 1 - and ± 3 -order sidebands), and (C) experimental data collected with BABA pulse sequence, $N = 4$, $\nu_R = 33$ kHz.

oscillation damping in the DQ build-up curve should be an effective method for detecting the presence of a distribution in the effective dipolar coupling.

As an experimental demonstration of the impact of a distribution in dipolar coupling, DQ ^1H MAS NMR spectra were obtained on a hydrated sodium hexaniobate containing 15 H_2O molecules per unit cell (Fig. 4C) [26]. For this sample it is assumed that all H_2O molecules have the same ^1H – ^1H distance and that differences in H_2O dynamics give rise to a distribution in the effective dipolar coupling. For rigid water a dipolar coupling of 33.4 kHz is expected using a ^1H – ^1H distance of 1.54 Å in Eq. (2) [28]. The simulations showing the best fit based on the lower-order sidebands (± 1 and ± 3), or the higher sideband ratios (± 7 and ± 9) are shown in Figs. 4A and B. From these simulations the effective (dynamically averaged) dipolar couplings are estimated to be 7 and 19 kHz, respectively. These results (Fig. 4) clearly show that the complete experimental ^1H DQ MAS NMR sideband manifold for the waters in the niobate material cannot be reproduced with a single dipolar coupling (i.e., a single dynamic order param-

eter), and attempts to use different sets of sideband ratios produces a large range of estimated dipolar couplings (a range of dynamics).

In Fig. 5 two experimental ^1H DQ MAS NMR spinning sideband patterns for sodium hexaniobate are displayed with the DQ simulations utilizing a Gaussian distribution in the effective dipolar coupling. Experimental spectra are shown for different excitation/reconversion times, $N = 2$ (Fig. 5B) and $N = 4$ (Fig. 5D). Comparing the experimental ratio of sideband intensities with the simulated curves in Fig. 2, a mean effective dipolar coupling $\overline{D}^{ij} = 23$ kHz and a standard deviation of $\sigma = 3.4$ kHz produced the best fit for the spectrum collected with $N = 4$ (Fig. 5C). This distribution is plotted below the spectra and shows that the mean effective dipolar coupling is shifted to a smaller value than that expected for rigid water (33.4 kHz). The simulation that best fits the experimental spectrum for $N = 2$ (Fig. 5A) yields $\overline{D}^{ij} = 23$ kHz and $\sigma = 3.0$ kHz, which agrees well with the values extracted from the experiment with $N = 4$. These results demonstrate that simulations of different experimental DQ excitation/

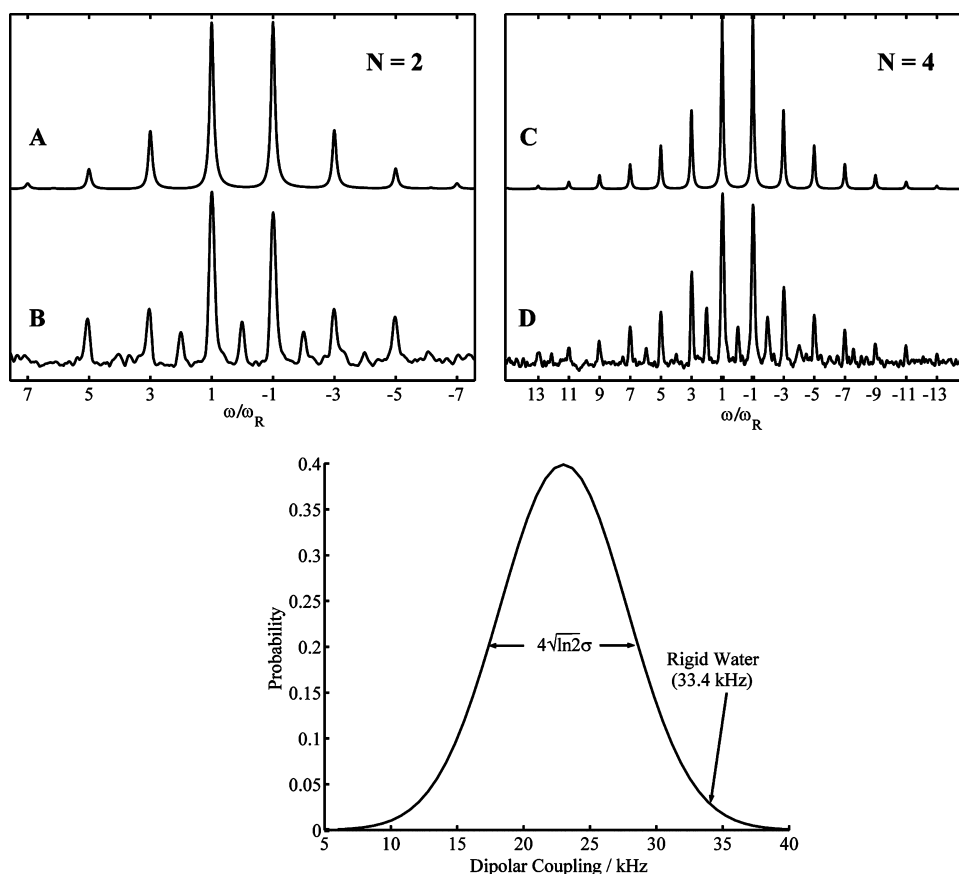


Fig. 5. ^1H DQ MAS NMR spectrum (F_1 slice taken at the water chemical shift) for sodium hexaniobate material containing 15 H_2O molecules. Simulation with (A) Gaussian distribution, $\overline{D}^{ij} = 23$ kHz and $\sigma = 3.0$ kHz and (B) experimental data collected with BABA pulse, $N = 2$, $\nu_R = 33$ kHz. Simulation with (C) Gaussian distribution, $\overline{D}^{ij} = 23$ kHz and $\sigma = 3.4$ kHz and (D) experimental data collected with BABA pulse, $N = 4$, $\nu_R = 33$ kHz. A plot of the Gaussian distribution of dipolar couplings used to perform the simulation in (C) is displayed below the experimental and simulated spectra.

reconversion times provide a consistent estimation of effective dipolar coupling and distribution. DQ spectra for shorter excitation times, $N = 1$, revealed only the ± 1 and ± 3 sidebands, and did not provide a very strong constraint for the determination of a unique effective dipolar coupling and distribution. Unfortunately, longer excitation/reconversion times ($N > 4$) were not attempted due to T_2 limitations.

These simulations of the experiment clearly indicate that a distribution in H_2O mobility is present. For this material H_2O is not confined to a small pore or channel, but instead is associated with the surface of the niobium oxide cluster, and therefore shows a wide range of motional dynamics producing a wide distribution in effective dipolar coupling [26]. Analysis of these distributions allows a measure of the dynamical motions (averaging process) occurring in these materials.

It should be noted that the appearance of even-order sidebands in the experimental DQ ^1H spectrum (Figs. 5B and D) is characteristic of multiple-spin interactions. In the presence of multi-spin dipolar interactions, or large chemical shift anisotropy (CSA), it is possible for the generation of even-ordered spinning sidebands through an evolution rotor modulation mechanism (ERM) [23]. This multi-spin effect may distort the odd-order sidebands, making it difficult to extract an accurate dipolar coupling. Multi-spin interactions have been proposed to explain the variation in ^1H DQ NMR sideband intensity for methyl groups in PDMS [14]. This influence of multi-spin interactions has also been described by Schnell and Spiess [23] where the degree of perturbation (ξ) on the two-spin approximation by an additional third spin is defined as:

$$\xi = \frac{2\pi D^{\text{pert}}}{\omega_{\text{R}}}, \quad (5)$$

where D^{pert} is the coupling strength of the perturbing spin and ω_{R} is the angular MAS spinning frequency. It was shown that for small perturbation, $\xi < 0.5$, an accurate dipolar coupling can still be extracted from simulation of the odd-order sidebands using the two-spin approximation given by Eq. (1) [23].

As an estimate to the impact of multi-spin interactions in the case of sodium hexaniobate, one can assume that the shortest ^1H – ^1H distance to a third spin is that of a hydrogen-bonded network of water (2.2 Å), which gives $\xi < 0.5$ at $\nu_{\text{R}} = 33$ kHz [29]. Therefore, as a first-approximation multi-spin effects will have a small impact on the odd-ordered sideband intensities, and the two-spin approximation is reasonable for the analysis of the experimental spinning sideband patterns for the hydrated sodium hexaniobate material. A more extensive investigation into multi-spin effects of surface adsorbed water species is ongoing. It is feasible that multi-spin interactions could produce large perturbations to the sideband intensities in some systems

indicating that both the impact of multi-spin effects and the influence of distributions in dipolar coupling strengths should always be addressed in the simulation of ^1H DQ MAS NMR spinning sideband patterns.

5. Conclusions

Distributions in homonuclear dipolar coupling greatly affect the appearance of the ^1H DQ MAS NMR spinning sideband spectrum. Specifically, an emphasis of the first-order sideband is observed as the standard deviation of the distribution is increased. The ratio of the higher-order sidebands with respect to the first-order sideband was calculated as a function of the mean dipolar coupling and standard deviation. These intensity ratios can be used to extract an average dipolar coupling and standard deviation by comparison to experimental sideband ratios. For small dipolar coupling only first-order sidebands are typically observed in the DQ spectrum. In this situation a distribution in the dipolar coupling can be detected in the damping of the DQ build-up curve. An experimental example using sodium hexaniobate showed that DQ simulations using a single dipolar coupling were unable to accurately reproduce the entire ^1H DQ MAS sideband pattern. The inclusion of a Gaussian distribution of effective dipolar couplings greatly improved the agreement between experiment and simulation. These results show that the effect of a distribution in dipolar coupling needs to be considered during simulation of ^1H DQ MAS NMR spinning sideband patterns; especially in amorphous and disordered systems where distributions of dipolar couplings (through either variation of internuclear distances or variations in motional averaging) are relevant.

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