Decoupling-induced recoupling in multiple-quantum magic-angle-spinning NMR spectra of quadrupolar nuclei

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Abstract

We report the observation of a new decoupling-induced recoupling phenomenon in multiple-quantum magic-angle-spinning (MQMAS) NMR spectra of half-integer quadrupolar nuclei. The origin of the effect is identical to the second-order recoupling between dipolar and anisotropic chemical shielding interactions under continuous-wave (CW) spin decoupling, which is first observed by Ernst et al. in the solid-state NMR spectra of spin-1/2 nuclei [J. Chem. Phys. 105 (1996) 3387].

1. Introduction

Since the introduction of the multiple-quantum magic-angle-spinning (MQMAS) methodology in 1995 [1,2], considerable attention has been drawn to the study of half-integer quadrupolar nuclei by solid-state nuclear magnetic resonance (NMR) spectroscopy. As a result, the long-standing lore of solid-state NMR that large quadrupolar interactions often lead to broad, featureless NMR line shapes has started to change. Since the MQMAS methodology provides a means of obtaining high resolution NMR spectra for half-integer quadrupolar nuclei, it is natural to anticipate that certain NMR phenomena and techniques that are common in solid-state NMR of spin-1/2 nuclei may be observable and useful in the study of half-integer quadrupolar nuclei. Indeed, it is this line of logic that has led to some recent developments. For example, the well-known cross polarization (CP) technique was incorporated into the MQMAS experiment [3–5]. The fine spectral features arising from indirect spin-spin (J) couplings [6,7] and residual dipolar couplings [8,9] were observed in MQMAS spectra. Very recently, rotational resonance (R2) involving half-integer quadrupolar nuclei was also reported [10].

Several years ago, Ernst et al. [11] reported a new second-order recoupling effect in solid-state NMR spectra of spin-1/2 nuclei. In particular, they demonstrated that, under the continuous wave (CW) spin decoupling condition, the heteronuclear dipolar interaction between two spin-1/2 nuclei can be reintroduced into MAS NMR spectra via a cross term between the dipolar and anisotropic chemical shielding interactions. Since this cross term consists of a sum of zeroth-, second- and fourth-rank tensors, it cannot be completely averaged by MAS, resulting in ‘residual’ dipolar broadening and splitting in the MAS spectra. Such ‘residual’ dipolar broadening and split-
ting are inversely proportional to the strength of the spin decoupling field. In this Letter, we report the first observation of this new decoupling-induced recoupling phenomenon in MQMAS NMR spectra of half-integer quadrupolar spins.

2. Theory

The fundamental theory of the second-order recoupling between dipolar and chemical shielding interactions under spin decoupling has been described in detail by Ernst et al. [11] using both the perturbation treatment and the average Hamiltonian theory. In this work, we take a slightly different approach. We have recently introduced a simple vector model approach in order to provide a unified physical picture for various residual dipolar coupling phenomena in solid-state NMR [12]. The second-order recoupling between dipolar and anisotropic chemical shielding interactions also belongs to this category, and therefore can be understood on the basis of the vector model approach.

For a spin pair consisting dipolar coupled \(^3\)O–\(^1\)H nuclei in the present case, the spin Hamiltonian under the spin decoupling condition can be written as:

\[
h^{-1}H = \omega_S S_z + \omega_{dd} \cdot 2 I_z S_z + \omega_{df} I_x + \omega_{csa} I_z, \tag{1}
\]

where \(\omega_S\) describes the NMR frequency for the \(S\)-spin, \(\omega_{dd}\) is the dipolar coupling between the \(S\)-and \(I\)-spins, \(\omega_{df}\) is the \(I\)-spin decoupling field strength, and \(\omega_{csa}\) describes the \(I\)-spin chemical shift anisotropy (CSA).

The vector model approach of treating the heteronuclear dipolar coupling [12] consists of four steps: (i) separate the \(I\)-spin and \(S\)-spin Hamiltonians, (ii) derive the spin eigenfunctions for each of the two spin Hamiltonians, (iii) calculate the expectation values for the spin angular momentum vectors \(\langle I \rangle\) and \(\langle S \rangle\), and (iv) combine \(\langle I \rangle\) and \(\langle S \rangle\) into the classical expression for the heteronuclear dipolar interaction. In the present case, we first focus on the \(I\)-spin part of the spin Hamiltonian,

\[
H_I = \omega_{df} I_x + \omega_{csa} I_z. \tag{2}
\]

Under the strong \(I\)-spin decoupling condition (\(\omega_{df} > \omega_{csa}\)), the CSA term can be treated as a perturbation. In the absence of this perturbation term, the two spin eigenstates of \(H_I\) are:

\[
\frac{1}{\sqrt{2}} (|+1/2\rangle \pm |-1/2\rangle) \quad \tag{3}
\]

With the vector model approach, we need to calculate the expectation values for the \(I\)-spin angular momentum from Eq. (3):

\[
\langle I_x \rangle = \pm \frac{1}{2}, \quad \langle I_y \rangle = 0, \quad \langle I_z \rangle = 0. \quad \tag{4}
\]

The above result indicates that the \(I\)-spins are polarized along the direction of the spin decoupling RF field, i.e., the \(x\)-direction. Under such circumstances, the dipolar splitting in the \(S\)-spin spectra vanishes:

\[
h^{-1}E_{DD} = \omega_{df} \cdot 2 \langle I_z \rangle = 0. \tag{5}
\]

Therefore, the dipolar interaction between \(I\) and \(S\)-spins is completely ‘removed’, leading to spin decoupling. The corresponding spin vector model is illustrated in Fig. 1A.

In the presence of the \(I\)-spin CSA perturbation term, the spin eigenstates for \(H_I\) are modified to:

\[
|+1/2\rangle = a|+1/2\rangle + b|-1/2\rangle, \tag{6}
\]

\[
|-1/2\rangle = b|+1/2\rangle - a|-1/2\rangle, \tag{7}
\]

Fig. 1. Vector model presentations for an \(I–S\) spin system under \(I\)-spin decoupling. (A) \(S = \frac{1}{2} \), without \(I\)-spin dipolar/CSA cross interaction, (B) \(S = \frac{1}{2} \) with \(I\)-spin dipolar/CSA cross interaction, (C) \(S > \frac{1}{2} \), without \(I\)-spin dipolar/CSA cross interaction, and (D) \(S > \frac{1}{2} \) with \(I\)-spin dipolar/CSA cross interaction.
where

\[
a = \frac{\omega_{rt}}{\sqrt{\omega_{rt}^2 + \left(\sqrt{\omega_{rt}^2 + \omega_{csa}^2} - \omega_{csa}\right)^2}}, \quad b = \sqrt{1 - a^2}.
\]

(8)

Now the expectation value for \( I_s \) in the new modified eigenstates can be calculated by expanding \( a \) to the first-order term of \( \omega_{csa}/\omega_{rt} \):

\[
\langle + 1/2 | I_s | + 1/2 \rangle = \langle - 1/2 | I_s | - 1/2 \rangle = \frac{1}{2}(a^2 - b^2) = a^2 - \frac{1}{2}
\]

\[
\equiv \frac{\omega_{csa}}{2 \omega_{rt}}.
\]

(9)

Consequently, the dipolar splitting in the \( S \)-spin spectra becomes:

\[
h^{-1}E_{dd} = \omega_{dd} \cdot 2\langle I_s \rangle \equiv \pm \omega_{dd} \frac{\omega_{csa}}{\omega_{rt}}.
\]

(10)

The above equation is identical to that derived by Ernst et al. [11]. This is entirely expected since, as we have already emphasized in the previous work [12], the vector model approach is fundamentally identical to the perturbation theory treatment.

As Ernst et al. pointed out [11], the implication of Eq. (10) is that, since both dipolar and CSA interactions are second-rank tensors, the product of them leads to a sum of zeroth-, second- and fourth-rank tensors. Therefore, under MAS, the dipolar splitting of Eq. (10) will generally give rise to an isotropic splitting from the zeroth-rank tensor and a broadening due to the incomplete averaging of the fourth-rank tensor. Eq. (10) also predicts that both the spectral splitting and broadening in the \( S \)-spin spectra will be inversely proportional to the \( I \)-spin decoupling field strength. These key features of the second-order recoupling effect were corroborated experimentally in the \( ^{15} \text{N} \) NMR spectra of \( \text{HN} \left( \text{CD}_{3} \right)_{2} \text{Cl}^{+} \) [11].

In the present work, the observed \( S \)-spin is a half-integer quadrupolar nucleus. As we have mentioned previously [12], the relevant spin vectors in the MQMAS experiment are also parallel to the z-axis, as illustrated in Fig. 1B. Thus, the second-order recoupling effect should be essentially the same in cases where the observed spin is greater than \( \frac{1}{2} \). As a result, the aforementioned spectral features should also be observable in the solid-state NMR spectra of quadrupolar nuclei. However, the presence of second-order quadrupolar broadening in such spectra may be obscured by line broadening from other mechanisms. This is perhaps the reason why the second-order recoupling effect has not been reported for quadrupolar nuclei until now. It is worth noting that, during the multiple-quantum \((mQ)\) evolution period of the MQMAS experiment, the recoupling effect is amplified \( m \) times,

\[
h^{-1}E_{dd}(mQ) = \pm m \frac{\omega_{dd} \omega_{csa}}{\omega_{rt}}.
\]

(11)

Since Eq. (11) is identical to that for the isotropic chemical shift, the scaling of the recoupling effect in MQMAS spectra is similar to the chemical shift scaling [13,14].

3. Experimental

Sample preparation. Water \((^{17} \text{O} 25\% \text{ atom})\) was purchased from Trace Science International (Toronto, Ontario). \( \text{Ca}^{(17) \text{OH}}_2 \) was prepared by slow precipitation from \( \text{CaCl}_2 \) and \( \text{Na}^{17} \text{OH} \) solutions followed by washing with water and drying at 120°C for 24 h.

Solid-state NMR. Solid-state \( ^{17} \text{O} \) NMR spectra were recorded on Bruker Avance-500 spectrometer operating at 500.13 and 67.8 MHz for \( ^1 \text{H} \) and \( ^{17} \text{O} \) nuclei, respectively. A polycrystalline sample of \( \text{Ca}^{(17) \text{OH}}_2 \) was packed into a zirconium oxide rotor (4 mm o.d.). The sample spinning frequency was 10 kHz. A recycle time of 20 s was used in the \( ^{17} \text{O} \) MAS experiments. In the \( ^{17} \text{O} \) MQMAS experiments, the two-pulse sequence with a z-filter [15] was used to obtain the States-type hypercomplex 2D data for phase-sensitive 2D spectra. The pulse width for the first and second pulses was 4.5 and 1.5 μs, respectively. In each MQMAS experiment, a total of 64 \( t_1 \) increments were recorded. For each \( t_1 \) increment, 360 scans were accumulated with a recycle delay of 5 s. A liquid sample of \( \text{H}_2 \text{O} \) (25% \( ^{17} \text{O} \) atom) was used for RF power calibration as well as for chemical shift referencing.

4. Results and discussion

Fig. 2 shows a series of experimental central-transition \( ^{17} \text{O} \) MAS spectra of \( \text{Ca}^{(17) \text{OH}}_2 \) at different \( ^1 \text{H} \)
decoupling power levels. At the highest $^1$H decoupling level, the $^{17}$O MAS spectrum exhibits a typical line shape arising from the second-order quadrupolar interaction. It is straightforward to analyze this second-order quadrupolar NMR line shape. Following $^{17}$O NMR parameters were obtained: $\delta_{\text{iso}} = 67$ ppm, $e^2qQ/h = 6.5$ MHz, and $\eta = 0$. These parameters are in good agreement with the values previously reported for Ca(OH)$_2$ [16,17].

It is also seen from Fig. 2 that, as the $^1$H decoupling power is decreased, the $^{17}$O MAS NMR spectra become broadened. At $\omega_{\text{rf}}/(2\pi) = 40$ kHz, the $^{17}$O MAS spectrum begins to lose its characteristic second-order quadrupolar line shape. However, except for the broadening effect, it is not clear whether the decrease in $^1$H decoupling power causes any additional change of the $^{17}$O NMR line shape.

Fig. 3 shows the 2D contour plots of $^{17}$O MQMAS spectra at different $^1$H decoupling power levels. Since these 2D NMR spectra were obtained with the shear Fourier transformation, the $F_1$ dimension corresponds to the so-called ‘isotropic’ axis. It is clearly seen from Fig. 3 that as the $^1$H decoupling power is reduced, the width of the 2D signal along the ‘isotropic’ axis becomes severely broadened. The line-width changes are better seen from the corresponding 1D isotropic MQMAS spectra, as shown in Fig. 4. At a very high $^1$H decoupling level, $\omega_{\text{rf}}/(2\pi) = 90$ kHz, the isotropic MQMAS spectrum of Ca($^{17}$OH)$_2$ exhibits a sharp peak whose line-width is approximately 625 Hz; see Fig. 4A. As the $^1$H decoupling power is reduced to 71 kHz, the isotropic peak broadens to approximately 937 Hz (Fig. 4B). At an even lower $^1$H decoupling power level,
Fig. 4. 1D $^{17}$O MQMAS spectra of Ca(OH)$_2$ at different $^1$H decoupling power levels. The decoupling field strength was (A) 90 kHz, (B) 71 kHz, (C) 56 kHz and (D) 40 kHz.

At 56 kHz, the 1D $^{17}$O MQMAS spectrum exhibits a doublet structure with a splitting of approximately 469 Hz. Finally, when $\omega_d/2\pi = 40$ kHz, a broad doublet is observed whose splitting is approximately 600 Hz with a total line width of 2109 Hz. Attempts to acquire $^{17}$O MQMAS spectra without $^1$H decoupling were unsuccessful.

In Fig. 5, the experimental spectral splittings and line widths are plotted against the inverse of the $^1$H decoupling field strength, $2\pi/\omega_d$. As expected from Eq. (10), both the splitting and the line width decrease linearly with $2\pi/\omega_d$. This observation is in excellent agreement with that of Ernst et al. in the $^{15}$N spectra of [HN(CD$_3$)$_3$] $^+$ Cl$^-$ [11].

Theoretically, both the spectral splitting and the line width of the 1D isotropic MQMAS spectra can be calculated according to the time average of the dipolar splitting (Eq. (10)) and a scaling factor arising from the MQMAS experiment [13,14]. Therefore, once the time averaging of the dipolar splitting is relevant.

$$\langle h^{-1}E_{1D}\rangle = 2 \left( \frac{\omega_d(t) \times \omega_{ca}(t)}{\omega_d} \right)$$

$$= 2\left( \frac{\omega_d(t) \times \omega_{ca}(t)}{\omega_d} \right). \quad (12)$$

To understand quantitatively the observed spectral splitting and line width, we utilized a residual $^1$H NMR approach [18] to determine the $^1$H chemical shift tensor for Ca(OH)$_2$. We obtained the following results for the $^1$H chemical shift tensor in Ca(OH)$_2$: $\delta_1 = \delta_2 = 8 \pm 1$ ppm, and $\delta_3 = -3 \pm 1$ ppm. This is very similar to an early report by Schreiber and Vaughan [19]. At 11.75 T, this $^1$H CSA corresponds to 5.5 kHz. The $^1$H–$^{17}$O dipolar coupling constant, $\omega_d/(2\pi)$, is calculated to be 16 kHz for an O–H separation of 0.984 Å in Ca(OH)$_2$ [20]. Interestingly, the $^{17}$O–$^1$H spin system in Ca(OH)$_2$ is remarkably similar to the $^{15}$N–$^1$H spin system in [HN(CD$_3$)$_3$] $^+$ Cl$^-$ which exhibits a $^1$H CSA of 6.0 kHz at 7.05 T and a $^{15}$N–$^1$H dipolar coupling constant of 20 kHz. In both cases, the dipolar and

Fig. 5. Experimental line width (filled circles, $R^2 = 0.9977$) and spectral splitting (open squares, $R^2 = 0.9456$) of the 1D isotropic $^{17}$O MQMAS spectra of Ca(OH)$_2$ versus the inverse of the $^1$H decoupling field strength.
chemical shielding tensors are axially symmetric and coincident. Therefore, the observed spectral features in the isotropic $^{17}\text{O}$ MQMAS spectra of Ca(OH)$_2$ can be compared directly with the numerical simulations of Ernst et al. [11]. We found an excellent agreement between our observations and the theoretical predictions of Ernst et al. [11], suggesting a common origin of the recoupling effects. Interestingly, the observed residual line broadening can be satisfactorily accounted for by considering only the second-order recoupling effect, which indicates that the first-order heteronuclear dipolar interaction is negligible under the present experimental conditions. This also means that a combination of 10 kHz MAS with 40 kHz spin decoupling is sufficient to remove the first-order $^{17}\text{O}$–$^1\text{H}$ heteronuclear dipolar effect in solid Ca(OH)$_2$.

At this point, it is also worth discussing further to what extent the second-order recoupling effect may influence the resolution in $^{17}\text{O}$ MQMAS spectra for organic compounds. Typical $^1\text{H}$ CSAs in organic compounds may be on the order of 20 ppm [21], which corresponds to $\omega_{\text{CSA}}/(2\pi) = 12$ kHz at $B_0 = 14.1$ T (600 MHz for $^1\text{H}$). Suppose that $\omega_B/(2\pi) = 10$ kHz and $\omega_d/(2\pi) = 100$ kHz. The spectral splitting predicted by Eq. (12) will on the order of 800 Hz. Increasing the $^1\text{H}$ decoupling field strength to $\omega_d/(2\pi) = 200$ kHz will reduce the splitting to 400 Hz. An alternative approach to CW spin decoupling is the recently developed TPPM technique [22]. Ernst et al. [11] demonstrated that TPPM is more effective in eliminating the broadening from the second-order dipolar/CSA recoupling effect. Massiot and co-workers [23] also employed the TPPM decoupling scheme in their MQMAS experiments and obtained spectral resolution superior to CW decoupling.

5. Conclusions

We have reported the observation of a new decoupling-induced recoupling phenomenon in MQMAS spectra for half-integer quadrupolar nuclei. The origin of the effect is identical to that described by Ernst et al. for spin-1/2 nuclei [11]. In cases where the dipolar interaction between the observed quadrupolar nucleus and $^1\text{H}$ is strong, the isotropic MQMAS spectra may exhibit severe line broadening or even splitting as a result of the recoupling effect between dipolar and chemical shift tensors. Using a vector model approach, we have provided a clear picture about this type of recoupling effect.

For half-integer quadrupolar nuclei, it is always desirable to perform MQMAS experiments at the highest magnetic field possible. Since both the spectral broadening and the splitting from the decoupling-induced recoupling effect are proportional to the applied magnetic field (through the CSA term), it is necessary to apply either very high power CW decoupling or alternative decoupling schemes such as TPPM to achieve high resolution in MQMAS spectra. It is anticipated that this type of recoupling effect will be important for quadrupolar nuclei such as $^{17}\text{O}$, $^{11}\text{B}$ and $^{27}\text{Al}$ for which strong dipolar couplings to $^1\text{H}$ are likely to occur.

For highly crystalline compounds, this decoupling-induced recoupling effect may be one of the limiting factors for the ultimate resolution achievable by MQMAS. It may also be possible that useful structural information can be extracted from the spectral features due to the second-order recoupling effect.

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