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Reconsideration of the NMR three-pulse responses of methyl protons in $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$

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Abstract. The response of triads of strongly coupled spin- $\frac{1}{2}$ nuclei to the generalized Goldman–Shen pulse sequence $(\alpha)_\phi - \tau_1 - (\alpha)_{\phi+180^\circ} - \tau_2 - (\beta)_{0^\circ}$ is reconsidered by taking into account the spin diffusion between the equidistant energy-level pairs of the spin-rotor system during the time τ_2 . The refined theory gives quantitatively correct model responses and sheds new light on the discrepancy between the previous theory for an ensemble of isolated triads and the analogous theory for pairs of coupled triads, in the limit of no coupling. Theoretical three-pulse spectra are compared with experimental responses of the tunnelling methyl protons in a $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ single crystal at 30 K.

1. Introduction

The original Goldman–Shen three-pulse sequence, $90^\circ_0 - \tau_1 - 90^\circ_{180^\circ} - \tau_2 - 90^\circ_0$, measures the transfer of Zeeman energy between nuclei experiencing the local field differently. The interval τ_1 between the oppositely phased resonant RF pulses of the flip angle 90° is adjusted to dephase the more-coupled nuclear spins so much that, at the beginning of the period τ_2 , only the less-coupled spins have magnetization left. The re-establishment of the internal equilibrium of the spin system during the variable time τ_2 is observed by the final pulse. Goldman and Shen [1] used the method to study cross relaxation between the fast- and slow-moving fluorine nuclei in LaF_3 . Punkkinen and co-workers [2] discovered its application to tunnelling ammonium ions below the linewidth transition temperature, where the magnetic-dipolar couplings between the protons belonging to ions of a certain rotational symmetry still average to zero. In this application the sequence measures the time taken by the magnetization transfer from one symmetry species to another.

In our previous papers [3–5] we calculated the effect of the more general sequence, $(\alpha)_\phi - \tau_1 - (\alpha)_{\phi+180^\circ} - \tau_2 - (\beta)_{0^\circ}$, on an ensemble of rotating triads of spin- $\frac{1}{2}$ nuclei, e.g. protons in solids containing CH_3 or NH_3 groups. Our model [4], which assumed fast transverse relaxation but no spin diffusion during the interval τ_2 , predicted the response shapes correctly but gave larger absolute amplitudes than is observed in $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ at 30 K. Later, the τ_2 dependence of the response was used to measure spin-diffusion rates in methyl compounds [5, 6]. A recent response calculation [7] for the system of pairs of coupled spin- $\frac{1}{2}$ triads conflicts, in the limiting case of no coupling, with the previous model for isolated triads but fits better with the experiment. The conflict is caused by the approximate treatment of the evolution during τ_2 in the two different representations of the system.

In this paper we show how the contradictory theoretical results can be interpreted, as the pairs model implicitly includes a certain degree of spin diffusion. By taking the spin

diffusion explicitly into account, the calculated responses can be fitted quantitatively to the $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ responses.

2. Theory

The eight eigenstates of the system of three nuclear $\frac{1}{2}$ -spins forming an equilateral triangle and performing rotational tunnelling or reorienting quickly relative to the NMR linewidth are labelled by $X_m = E^a_{\pm 1/2}, E^b_{\pm 1/2}, A_{\pm 3/2}$ and $A_{\pm 1/2}$ according to the C_3 point-group symmetry and the z component of the total nuclear spin [8]. The dipole-dipole interaction between the three nuclei shifts the $A_{\pm 3/2}$ levels upwards and the $A_{\pm 1/2}$ levels downwards by $\hbar\omega_d = (\mu_0/4\pi)(3\gamma^2\hbar^2/8r^3)(3\cos^2\theta - 1)$, where r is the distance between the nuclei in the triangle, θ the angle between its threefold reorientation axis and the Zeeman field, and γ the magnetogyric ratio [9]. The NMR spectrum consists of the central resonance and the satellites separated from it by $\pm 2\omega_d$. In equilibrium, the intensities of the three lines behave as $M_+ : M_c : M_- = 1 : 2 : 1$, unless the tunnel splitting between the A and E levels, $\hbar\omega_t$, is comparable to $k_B T$.

The excess populations, n_{X_m} , of the eight energy levels can be combined into seven independent quantities u, v, z, y, e, f and s defined by equation (6) in [5]. The quantities u, v and e do not appear in the NMR spectrum, z is proportional to the Zeeman energy and y to the dipolar energy. The quantity f is related to the spin-temperature difference between the equidistant energy-level pairs and s to the difference between the non-equidistant pairs:

$$\begin{aligned} f &= n_{E^a_{\frac{1}{2}}} - n_{E^a_{-\frac{1}{2}}} + n_{E^b_{\frac{1}{2}}} - n_{E^b_{-\frac{1}{2}}} - 2n_{A_{\frac{1}{2}}} + 2n_{A_{-\frac{1}{2}}} \\ s &= n_{E^a_{\frac{1}{2}}} - n_{E^a_{-\frac{1}{2}}} + n_{E^b_{\frac{1}{2}}} - n_{E^b_{-\frac{1}{2}}} - n_{A_{\frac{3}{2}}} + n_{A_{\frac{1}{2}}} - n_{A_{-\frac{1}{2}}} + n_{A_{-\frac{3}{2}}}. \end{aligned} \quad (1)$$

When a resonant RF pulse of the flip angle β is applied to the three-spin system in an arbitrary statistical mixture of the eigenstates, the spectral amplitudes of the free induction decay are given by [3-5]

$$\begin{aligned} M_{\pm}(\beta) &= \frac{1}{32}[(8z - f - 3s)\sin\beta \pm 12y\sin 2\beta + 3(f - s)\sin 3\beta] \\ M_c(\beta) &= \frac{1}{32}[(16z + 2f + 6s)\sin\beta - 6(f - s)\sin 3\beta]. \end{aligned} \quad (2)$$

From these expressions we can solve the quantities

$$\begin{aligned} z &= [M_c(\beta) + M_+(\beta) + M_-(\beta)]/\sin\beta \\ y &= \frac{4}{3}[M_+(\beta) - M_-(\beta)]/\sin 2\beta \\ f &= 2[M_c(90^\circ) - M_+(90^\circ) - M_-(90^\circ)] \\ s &= \sqrt{6}[M_c(54.7^\circ) - M_+(54.7^\circ) - M_-(54.7^\circ)]. \end{aligned} \quad (3)$$

In an internal equilibrium of the spin system (i.e. a common spin temperature over the Zeeman levels) $f = s \approx 0$, if $\hbar\omega_t \ll k_B T$ (for $\hbar\omega_t \ll k_B T$, see (7) in [5]), and $y \ll z$.

When applied to the three-spin system, the pulse sequence $(\alpha)_\phi - \tau_1 - (\alpha)_{\phi+180^\circ} - \tau_2 - (\beta)_\phi$ utilizes coherent precession under the strong dipolar coupling rather than irreversible dephasing as does the original Goldman-Shen method. Here, the first of the three non-selective pulses converts the longitudinal polarization to the coherent superpositions of the states of the same symmetry. During τ_1 , the A-type coherences are affected by the coupling ω_d . Then the second pulse partly converts coherences back to the longitudinal order. During τ_2 , the remaining coherences decay, so that the response by the final pulse reflects only the

existing level-population differences. If initially $f = s = y = 0$ (for the general case, see e.g. (12) in [5]), the spectrum of the response is given by [4]

$$M_+ = M_- = A - B \quad M_c = 2(A + B) \quad (4)$$

$$A = [1 - \sin^2(\omega_d \tau_1) \sin^2 \alpha] \sin \beta \quad (5)$$

$$B = \sin^2(\omega_d \tau_1) \left[\left(\frac{1}{2} \sin^2 \alpha - \frac{3}{8} \sin^4 \alpha \right) \sin \beta + \left(\frac{3}{2} \sin^2 \alpha - \frac{15}{8} \sin^4 \alpha \right) \sin 3\beta \right]. \quad (6)$$

The amplitudes were here scaled to give $M_c + M_+ + M_- = 2 + 1 + 1$ by a single 90° pulse or by a sequence with $\alpha = 0^\circ$ and $\beta = 90^\circ$. The absolute phase of the first two pulses, ϕ , and the period, τ_2 , do not appear in these expressions, as τ_2 is assumed to exceed the phase memory of the system though to be too short for any process to modify the energy-level populations. Formally, the first assumption means an ignorance of the off-diagonal elements of the density matrix between the second and third pulse. Because no transverse relaxation is included in our model, those terms would oscillate forever.

The spectrum [10, 11] as well as the pulse responses [7] of the system of the six spin- $\frac{1}{2}$ nuclei forming a pair of rotating triads can be analytically calculated, if the axes of the triads are parallel. In that case the only new parameter entering into expressions is $\omega_{dp} = (\mu_0/4\pi)(\gamma^2 \hbar/R^3)(1 - 3 \cos^2 \Theta)$, where R is the average distance between the nuclei belonging to the neighbouring triads and Θ is the angle made by the Zeeman field with the axis joining the centres of the triangles. For coaxial triads $\Theta = \theta$. As $\omega_{dp} = 0$ corresponds to the vanishing dipole-dipole interaction between the triads ($R = \infty$ or $\Theta = 54.7^\circ$), one would expect the three-pulse response of the pair in that limiting case to become identical with (4)–(6). However, instead of (6) one obtains [7]

$$B = \sin^2(\omega_d \tau_1) \left[\left(\frac{19}{32} \sin^2 \alpha - \frac{33}{64} \sin^4 \alpha \right) \sin \beta + \left(\frac{39}{32} \sin^2 \alpha - \frac{93}{64} \sin^4 \alpha \right) \sin 3\beta \right]. \quad (7)$$

These two responses are identical only if $\alpha = 0^\circ$ (equilibrium unaltered) or $\alpha = 54.7^\circ$. Generally, for all α and τ_1 , the substitution of (4)–(6) or (4), (5) and (7) into (3) gives the same value of z and s , but f by (7) is $5/8$ of that by (6). It is as if some spin diffusion involving the equidistant energy-level pairs had taken place before the third pulse.

Formally, the contradiction is due to the different representations used in the derivations together with the rejection of the off-diagonal elements of the density matrix before the application of the third pulse. The calculated signals deviate, because the density matrix of six $\frac{1}{2}$ -spins is generally not simultaneously diagonal in the eigenbase [11] of a pair of interacting triads for $\omega_{dp} = 0$ and in the base of the products of the eigenstates of an isolated triad. (In the special case of an internal equilibrium of the spin system, or Boltzmann populations corresponding to an arbitrary Zeeman temperature at a high lattice temperature, assumed for example before the application of our pulse sequence, the density matrix is diagonal in both representations.) Such a representation dependence is possible, when the subsystems have equidistant energy-level pairs as $E_{\pm 1/2}^A$ and $A_{\pm 1/2}$ producing to the dipolar-coupled total system states of the type $(|A_{1/2}, E_{-1/2}^A\rangle \pm |A_{-1/2}, E_{1/2}^A\rangle)/\sqrt{2}$. It would not arise, for example, in the case of a pair of two $\frac{3}{2}$ -spins. On the other hand, if the off-diagonal elements are preserved and the density matrix evolves during τ_2 without loss of coherence under the dipolar coupling, the response obtained does not depend on the representation used and the contradiction at $\omega_{dp} = 0$ does not arise (see appendix). Moreover, if the zero-quantum coherences (superpositions of the states of the same Zeeman energy) are preserved while the other off-diagonal elements of the density matrix in the eigenbase of the coupled triads are not taken into account, one obtains a response that agrees with the expressions (4)–(6) in the case of $\omega_{dp} = 0$. (Note that the zero-quantum coherences do not arise in the eigenbase of a single triad, since they would involve states

of different symmetry.) These arguments were checked by calculating the coupled-triads responses for arbitrary τ_1 and τ_2 in the case $\alpha = \beta = 90^\circ$ and $\phi = 0^\circ$.

However, we are not interested in pulse sequences with τ_2 of the order of the phase-memory time. In our case, the coherences have not totally decayed but there are no grounds for keeping some of them while ignoring the others. The proper treatment of the decrease of the off-diagonal elements of the density matrix would be a troublesome task. According to our observations on the difference between the expressions (6) and (7), the task can be circumvented by instead letting the diagonal elements to decay appropriately.

Spin diffusion is the process which, through dipolar flip-flop transitions, modifies the level populations of a spin system towards an internal equilibrium. In the system of rapidly rotating spin- $\frac{1}{2}$ triads, spin diffusion can change neither z , u nor v , and even y only very limitedly [5, 12]. A detailed calculation [5] of the process in a rigid solid containing equivalently oriented rotating triads shows that, while e decays independently to zero, the diffusion of f and s are generally coupled. In samples, where the triads are far away from each other, f and s decay independently of each other and f much faster than s , i.e. $f(t) = f(0) \exp(-t/\tau_f)$ and $s(t) = s(0) \exp(-t/\tau_s) \approx s(0)$ for $t \ll \tau_s$. (Expressions relating the time constants to the crystal structure are given by (5) and (9) in [5].) The substitution of $z(\tau_2) = z(0)$, $y(\tau_2) = y(0)$, $f(\tau_2) = f(0) \exp(-\tau_2/\tau_f)$ and $s(\tau_2) = s(0)$, with $z(0)$, $y(0)$, $f(0)$ and $s(0)$ given by (3) and (4)–(6), into (2) yields the third set of spectral amplitudes with (4) and (5) unchanged but (6) replaced by

$$B = \sin^2(\omega_d \tau_1) \left[\left(-\frac{1}{4} \sin^2 \alpha + \frac{3}{8} \sin^4 \alpha \right) \sin \beta + \left(\frac{3}{4} \sin^2 \alpha - \frac{9}{8} \sin^4 \alpha \right) \sin 3\beta \right] \exp(-\tau_2/\tau_f) \\ + \sin^2(\omega_d \tau_1) \left[\left(\frac{3}{4} \sin^2 \alpha - \frac{3}{4} \sin^4 \alpha \right) \sin \beta + \left(\frac{3}{4} \sin^2 \alpha - \frac{3}{4} \sin^4 \alpha \right) \sin 3\beta \right]. \quad (8)$$

By also taking into account the spin diffusion between the non-equidistant level pairs and the coupling between f and s , relevant for nearby triads, one obtains the fourth set, where the expression (6) is replaced by

$$B = \sin^2(\omega_d \tau_1) \left[\left(-\frac{1}{4} \sin^2 \alpha + \frac{3}{8} \sin^4 \alpha \right) \sin \beta + \left(\frac{3}{4} \sin^2 \alpha - \frac{9}{8} \sin^4 \alpha \right) \sin 3\beta \right] \exp(-\tau_2/\tau_f) \\ + \sin^2(\omega_d \tau_1) \left[\left(\frac{3}{4} \sin^2 \alpha - \frac{3}{4} \sin^4 \alpha \right) \sin \beta \right. \\ \left. + \left(\frac{3}{4} \sin^2 \alpha - \frac{3}{4} \sin^4 \alpha \right) \sin 3\beta \right] \exp(-\tau_2/\tau_s) \\ + \frac{1}{32} [(-f_+ + 3s_-) \sin \beta + (3f_+ + 3s_-) \sin 3\beta] \exp(-\tau_2/\tau_f) \\ + \frac{1}{32} [(f_+ - 3s_-) \sin \beta + (-3f_+ - 3s_-) \sin 3\beta] \exp(-\tau_2/\tau_s). \quad (9)$$

Here f_+ and s_- are constants that depend (via (10) in [5]) on $f(0)$, $s(0)$ and the distance between triads. If the triads are far away from each other, $f_+ \approx s_- \approx 0$.

The third set, given by (4), (5) and (8), agrees with the first set, (4)–(6), if $\tau_2 = 0$ or $\tau_f = \infty$, and, on the other hand, with the second set, (4), (5) and (7), if $\exp(-\tau_2/\tau_f) = 5/8$. One could calculate the three-pulse response by the original method for systems of a larger and larger number of coupled triads and one would obtain, in the limit of no coupling, single-triad responses, where the spin diffusion between the equidistant level pairs would seem to have taken place to a higher and higher degree, because a greater and greater part of the potential f -polarization is rejected with the zero-quantum coherences. The expressions of such responses would converge to the third set, provided $\exp(-\tau_2/\tau_f) = 0$. Therefore one should not expect identical responses at $\omega_{dp} = 0$ by such approximate models for an arbitrary τ_2/τ_f but rather for $\tau_2/\tau_f \rightarrow \infty$. The choice of the representation, irrespective of the coupling strength, fixes the boundary between the system and its surroundings. If more spins are included in the system, an increasingly large part of the potential longitudinal order

created by the pulse pair is related to the off-diagonal elements of the density matrix, but since there are then fewer spins in the surroundings to disturb the coherence, the rigorously calculated response would be independent of representation for an arbitrary τ_2 . Our refined model does not describe the τ_2 dependence of the response correctly in the range from $\tau_2 = 0$ to the phase-memory time, because the spin-diffusion rate equations used in the derivation of (8) and (9) assume a statistical mixture of the eight eigenstates. For a fixed τ_2 of any length, quantitatively correct responses can be formed by giving proper values to the parameters τ_f and τ_s .

3. Comparison with experiment

In real crystals containing tunnelling or rapidly reorienting triads of $\frac{1}{2}$ -spins (e.g. CH_3 or CF_3 groups) the triads are more often arranged in proximate pairs than distributed evenly and far away from each other. To test how a model describes the case of the vanishing interaction between the two triads, $\omega_{\text{dp}} = 0$, one should orientate the Zeeman field to give $\Theta = 54.7^\circ$, because it is not possible to put $R = \infty$. The models also require that all the triad axes are parallel, but in most such crystals the triads of the pair are coaxial, which means $\omega_{\text{d}} = 0$ for $\Theta = 54.7^\circ$ and which makes the three-pulse experiment non-applicable. A single crystal of sodium acetate trihydrate provides an exception.

First, we reanalyze the $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ experiments presented in [4]. The Zeeman field corresponding to the proton resonance frequency of 32.5 MHz was parallel to the crystalline c axis giving $\omega_{\text{dp}} \approx 0$ and $\omega_{\text{d}}/2\pi = 9.5$ kHz. At 30 K the methyl protons reorient quickly relative to the NMR linewidth and the effective tunnel splitting does not change the intensity ratios of the lines because $\hbar\omega_{\text{t}}/k_{\text{B}} = 0.05$ K \ll 30 K [13].

Figure 1 compares the three-pulse response amplitudes M_+ , M_- and M_c calculated by the various models with the measured amplitudes (spectral areas) of the satellites and the central resonance. (As (4) and (5) are valid for all the models, the four models are identified here by the expressions (6)–(9). The borderlines between the sections of the experimental spectrum are shown in [4], figure 2). The ordinate in figure 1(a) is the same ratio as in [4] and does not show much difference between the models. For that ratio, in the case of figure 1(d), all the models would give an identical curve (plotted in [4], figure 5). Figures 1(b)–(d) compare the absolute satellite area, $M_+ + M_-$, and show that (7) fits better than (6) while the best fit is obtained by (8) with $\exp(-\tau_2/\tau_f) = 0.3$. Since $\tau_2 = 0.1$ ms, the fit implies $\tau_f = 0.08$ ms. According to the measurements in [5], $\tau_f = 0.82$ ms, but there the time constant describes the time dependence of f from $\tau_2 = 0.25$ ms onwards. The experimental points for a larger value of τ_2 (open circles in figures 1(a) and 1(b)) show the effect of spin diffusion during the period between the second and third pulse. The impairment of the fit with increasing τ_1 in figure 1(c) is due to the loss of coherence between the first two pulses, which is not included in any of the models. The original spectra of the experiments in figures 1(a) and 1(b), and in 1(d) as well as their theoretical counterparts for the models (6) and (8) are plotted in figure 2.

Note that the decay of s is not involved in the previous experiments, as either $\alpha = 90^\circ$ or $\beta = 90^\circ$ in all of the $(\alpha)_\phi - \tau_1 - (\alpha)_{\phi+180^\circ} - \tau_2 - (\beta)_{0^\circ}$ sequences studied. Using the same experimental set-up, we measured the response to the sequence with $\beta = 20^\circ$ for $\alpha = 0^\circ, \dots, 90^\circ$, varying also τ_2 . Figure 3 shows the results for two values of τ_2 . Besides the f decay caused by spin diffusion between the equidistant level pairs, there seems also to have taken place some decay of s during $\tau_2 = 0.1$ ms. The relatively slow decay of s from the time 0.1 ms onwards is in accordance with $\tau_s = 40$ ms measured in [5], while the

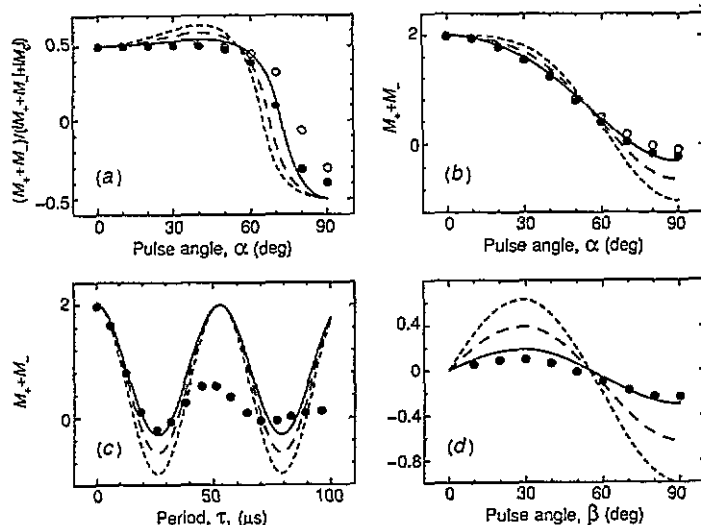


Figure 1. Comparison of calculated three-pulse responses with measured spectral areas in a $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ single crystal at 30 K. The ordinate in (a) is the ratio $(M_+ + M_-)/(|M_+ + M_-| + |M_c|)$ and in (b)–(d) the absolute satellite area $M_+ + M_-$ scaled to give $M_c + M_+ + M_- = 2 + 1 + 1$ by a single 90° pulse. The pulse sequences are ((a) and (b)) $(\alpha)_{0^\circ} - 26 \mu\text{s} - (\alpha)_{180^\circ} - \tau_2 - 90^\circ_{0^\circ}$, (c) $90^\circ_{0^\circ} - \tau_1 - 90^\circ_{180^\circ} - \tau_2 - 90^\circ_{0^\circ}$ and (d) $90^\circ_{0^\circ} - 26 \mu\text{s} - 90^\circ_{180^\circ} - \tau_2 - (\beta)_{0^\circ}$. The full circles refer to experiments with $\tau_2 = 100 \mu\text{s}$ and the open circles to $\tau_2 = 200 \mu\text{s}$. The short-dash broken curves are calculated using equation (6), the long-dash broken curves using (7) and the full curves using (8) with $\exp(-\tau_2/\tau_f) = 0.3$. The value $26 \mu\text{s}$ of τ_1 corresponds to $\tau_1\omega_d \approx \pi/2$.

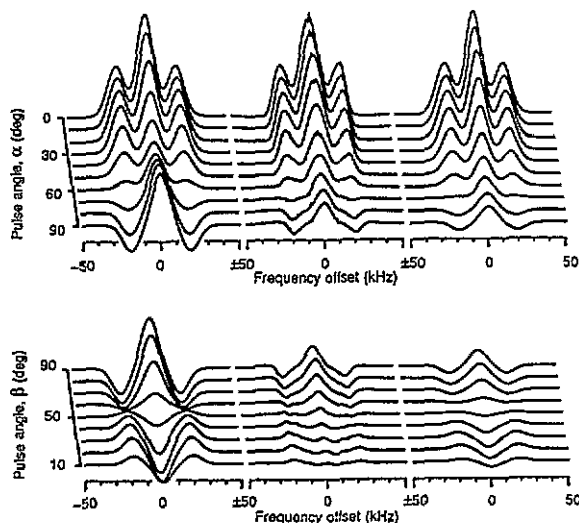


Figure 2. Simulated and experimental proton spectra of a $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ single crystal by the pulse sequence $(\alpha)_{0^\circ} - 26 \mu\text{s} - (\alpha)_{180^\circ} - 100 \mu\text{s} - 90^\circ_{0^\circ}$ for different pulse angles $\alpha = 0^\circ, \dots, 90^\circ$ (upper plots) and $90^\circ_{0^\circ} - 26 \mu\text{s} - 90^\circ_{180^\circ} - 100 \mu\text{s} - (\beta)_{0^\circ}$ for $\beta = 90^\circ, \dots, 10^\circ$ (lower plots). The experimental spectra (middle) underlie the full circles in figure 1. The left spectra are calculated using equation (6) as the short-dash broken curves in figure 1 and the right spectra using (8) with $\exp(-\tau_2/\tau_f) = 0.3$ as the full curves in figure 1. The theoretical spectral lines are broadened by a Gaussian curve with a width (FWHM) of 12.5 kHz.

decay of f is already finished in 2 ms. Because the s decay is related to the spin diffusion between the non-equidistant level pairs, the reduced value of s , after the shortest period τ_2 , cannot be justified by the same reasoning as that for f . The small but non-vanishing coupling between s and f (cf. the model (9)) could provide an explanation. Furthermore,

the true values of s and f for $\tau_2 = 0$ are certainly smaller than the calculated ones due to the loss of coherence during τ_1 , the imperfections of the first two pulses, etc.

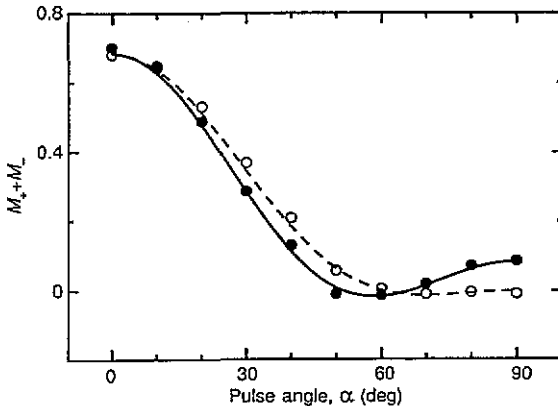


Figure 3. The spectral satellite area $M_+ + M_-$ in a $\text{CH}_3\text{COONa}\cdot 3\text{D}_2\text{O}$ single crystal at 30 K by the pulse sequence $(\alpha)_{0^\circ} - 26 \mu\text{s} - (\alpha)_{180^\circ} - \tau_2 - 20^\circ$, with $\tau_2 = 0.1$ ms (full circles) and $\tau_2 = 5$ ms (open circles). The fits are calculated using (9) with $\exp(-\tau_2/\tau_f) = 0.15$ and $\exp(-\tau_2/\tau_s) = 0.6$ (full curve) and $\exp(-\tau_2/\tau_f) = 0$ and $\exp(-\tau_2/\tau_s) = 0.5$ (broken curve). The ordinate units are as in figure 1.

4. Conclusions

The essential achievement of the present study is the clarification of the apparent contradiction between the three-pulse response spectra calculated for isolated triads of spin- $\frac{1}{2}$ nuclei (model (6)) and for pairwise-coupled triads in the no-coupling limit (model (7)). The contradiction is caused by the conventional assumption that during τ_2 the coherences decay while the longitudinal order remains unchanged. No contradiction appears, (i) in the unlikely case that a certain part of the coherences survive alone (model (6)), or in the two extreme cases treated rigorously: (ii) τ_2 is much shorter than all decay times (see appendix) and (iii) τ_2 exceeds the time required for the transverse relaxation as well as that for the spin diffusion between the equidistant energy-level pairs (model (8) for $\tau_2 \rightarrow \infty$). In the intermediate cases a rigorous treatment can be avoided, and a quantitative agreement between the calculated and observed responses can be achieved, by including spin diffusion between the equidistant energy-level pairs (model (8)) as well as between the non-equidistant level pairs (model (9)).

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Appendix

The response of an isolated, rotating triad of spin- $\frac{1}{2}$ nuclei to the pulse sequence $(\alpha)_\phi - \tau_1 - (\alpha)_{\phi+180^\circ} - \tau_2 - (\beta)_{0^\circ}$, with $\phi = 0^\circ$ and τ_2 much shorter than the phase-memory time, is given by

$$M_+ = M_- = A - B \quad M_c = 2(A + B) \quad M'_+ = -M'_- = C \quad M'_c = 0$$

(A.1)

$$\begin{aligned}
 A = & \sin \beta + \sin^2(\omega_d \tau_1)(-\sin^2 \alpha \sin \beta - \sin \alpha \cos \alpha \cos \beta) \\
 & + \sin^2(\omega_d \tau_1) \sin^2(\omega_d \tau_2)(2 \sin \alpha - 3 \sin^3 \alpha) \cos \alpha \cos \beta \\
 & - 2 \sin(\omega_d \tau_1) \cos(\omega_d \tau_1) \sin(\omega_d \tau_2) \cos(\omega_d \tau_2) \sin \alpha \cos \alpha \cos \beta
 \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned}
 B = & \sin^2(\omega_d \tau_1) \left[\frac{1}{4} \sin^2 \alpha \sin \beta + \left(\frac{9}{4} \sin^2 \alpha - 3 \sin^4 \alpha \right) \sin 3\beta + \frac{1}{4} \sin \alpha \cos \alpha \cos \beta \right. \\
 & \left. + \left(\frac{3}{4} \sin \alpha - 3 \sin^3 \alpha \right) \cos \alpha \cos 3\beta \right] + \sin^2(\omega_d \tau_1) \sin^2(\omega_d \tau_2) \\
 & \times \left[\left(\frac{1}{2} \sin^2 \alpha - \frac{3}{4} \sin^4 \alpha \right) \sin \beta + \left(-\frac{3}{2} \sin^2 \alpha + \frac{9}{4} \sin^4 \alpha \right) \sin 3\beta \right. \\
 & \left. + \left(-\frac{1}{2} \sin \alpha + \frac{3}{4} \sin^3 \alpha \right) \cos \alpha \cos \beta + \left(-\frac{3}{2} \sin \alpha + \frac{9}{4} \sin^3 \alpha \right) \cos \alpha \cos 3\beta \right] \\
 & + \sin(\omega_d \tau_1) \cos(\omega_d \tau_1) \sin(\omega_d \tau_2) \cos(\omega_d \tau_2) \\
 & \times \left(-\frac{1}{2} \sin^2 \alpha \sin \beta + \frac{3}{2} \sin^2 \alpha \sin 3\beta + \frac{1}{2} \sin \alpha \cos \alpha \cos \beta \right. \\
 & \left. + \frac{3}{2} \sin \alpha \cos \alpha \cos 3\beta \right)
 \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned}
 C = & \sin^2(\omega_d \tau_1) \sin(\omega_d \tau_2) \cos(\omega_d \tau_2) \left[(-4 \sin^2 \alpha + 6 \sin^4 \alpha) \sin \beta \right. \\
 & \left. + (-4 \sin \alpha + 6 \sin^3 \alpha) \cos \alpha \cos \beta \right] \\
 & + \sin(\omega_d \tau_1) \cos(\omega_d \tau_1) \sin^2(\omega_d \tau_2) (-4 \sin^2 \alpha \sin \beta - 4 \sin \alpha \cos \alpha \cos \beta) \\
 & + \sin(\omega_d \tau_1) \cos(\omega_d \tau_1) (2 \sin^2 \alpha \sin \beta + 2 \sin \alpha \cos \alpha \cos \beta).
 \end{aligned} \quad (\text{A.4})$$

Here the amplitudes with a prime refer to the imaginary part of the spectrum obtained by the complex Fourier transform of the free induction decay following the third pulse. (The components $M'_{+, -, c}$ vanish in the case of the responses discussed in the text.)

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