NMR spin-echo responses in the ordered cubic phase of solid deuterium

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NMR spin echoes stimulated in the ordered cubic phase of solid D_2 by $90°$-τ-$90°_{90°}$ pulse sequences using nonrigid rotating 90° rf pulses are shown to be in quantitative agreement with the theoretical line shapes predicted from the intramolecular dipolar interaction between $I = 1$ nuclei on a rigid lattice when spectral attenuation of the 90° rf pulse power profile is properly taken into account. A single-particle theoretical model for the $I = 1$ component of cubic-D_2 solid echo, which neglects effects due to intermolecular dipolar interactions, is developed for the general case where nonrigid rotation of the $I = 1$ spin system is produced by both pulses in the echo creation sequence. The characteristic features of this model are demonstrated for the case of the solid-echo profile of 80% para-D_2 at 0.94 K, with the predicted attenuation of the signal-amplitude maximum at 2τ agreeing with the observed decrease within the precision measure of the experiment. In addition, the Fourier transform of the experimental echo profile of 80% para-D_2 at 1.4 K is found to be in good agreement with the published cw spectrum of Maraviglia *et al.*

I. INTRODUCTION

The NMR transient response of the solid hydrogens (H_2 or D_2) to a resonanat rf pulse sequence $90°$-τ-$90°_{90°}$, where τ, the time between pulses, is small compared with the spin-spin relaxation time T_2, gives rise to a "solid" echo at time $t = 2\tau$ after the first pulse which originates from the combined effect of the dipolar coupling between the proton (deuteron) spins and the interactions of the spin pairs themselves.[1-3] Since the intramolecular dipolar interactions are averaged over the rotational motion of the molecules, the relative contribution that intrapair effects make to the frequency spectrum of the solid-echo profiles is highly sensitive to the orientational state of the molecular system. In solids of greater than about 55% $J = 1$ angular momentum species, which exhibit a cooperative ordering of molecular axes[4-6] accompanied by a crystal phase change[7,8] at the order-disorder transition temperature T_λ,[9] these intrapair effects produce a fine structure of splitting of the dipolar spectrum.[10-13] This manifests itself in the solid-echo response by an oscillatory beat pattern, the period of which is a direct measure of the orientational order parameter[13,14] if the crystalline state of the sample is known. The unaveraged intramolecular component of the local dipolar field dominates the dipolar interactions in the ordered phase, so that in describing the properties of the solid-echo profiles the much weaker intermolecular interactions can be neglected. Echoes created under these general conditions have in the limit $\tau \to 0$ been theoretically shown[1-3,15,16] to have a functional form identical with that of the free-induction-decay (FID) signal.

Solid-echo techniques are of great practical importance in NMR measurements on the orientationally ordered hydrogens, because they allow the extrication of information not easily or unambiguously determinable from either steady-state line shape[17] or FID[18] analyses. The very slow thermal relaxation rates of the ordered phase, particularly in the high-concentration $J = 1$ alloys of cubic D_2, give rise to anamolous saturation behavior and low signal-to-noise ratios in a cw NMR experiment, which are minimized in a solid-echo study. In addition, the initial behavior of the FID for the very broad $I = 1$ cubic-phase absorption normally obscured by receiver dead time is retained via the rephasing and subsequent dephasing of signal about 2τ that characterizes the solid-echo envelope.

There is, however, another unique experimental problem that arises when pulsed techniques are applied in conjunction with the broad $I = 1$ linewidth and the very low temperatures required for stabilization of the cubic phase. Due to the extreme length and high resistance of the rf transmission lines required by the design and heat-input restrictions of practical cryogenic systems, inherent limitations in transmitted rf power result, necessitating the utilization of 90° rf pulses having an insufficient irradiative bandwidth to saturate the entire $I = 1$ spin system. Consequently, selective attenuation of the interrogated $I = 1$ echo signal brought about by the limited power distribution of

the experimental 90° rf pulses must be taken into account in interpreting the solid-hydrogen echo profiles.

The purpose of this report is to demonstrate that the $I=1$ cubic-D_2 solid echo stimulated by nonrigid rotating 90° rf pulses is in accord both experimentally and theoretically with spectra predicted for the intramolecular dipolar interactions between deuterons on a rigid lattice when proper account is taken of spectral attenuation due to rf power limitations. A single-particle theoretical model similar to that of Metzger and Gaines[1] is developed to describe the characteristic features of the nonrigid rotation echos which allows the $I=1$ frequency spectra extracted from the experimental echo signals to be compared with predicted $I=1$ absorption line shapes and published cw NMR data.

II. EXPERIMENTAL METHOD

The NMR spin echoes were observed with a broad-line spectrometer (Spin Lock Ltd. model CPS-2) using phase-coherent rf pulses and phase-sensitive detection at a crystal controlled frequency of 8.00 MHz. The nuclear induction signals stimulated by resonant $90°\text{-}\tau\text{-}90°_{90°}$ pulse sequences ($\tau \sim 0.2$ msec) were digitally recorded and stored on magnetic tape to allow further data processing. The spectrometer rf transmitter produced a 90° pulse for deuterons in 12.5 μsec, while the bandwidth of the receiver-detection system was ~0.5 MHz at −45 dB.

Since the time duration for a 90° pulse was significantly greater than the inverse linewidth of the $I=1$ cubic-phase absorption spectrum (~150 kHZ), a detailed knowledge of the power spectrum for the rf oscillation[19,20] becomes an important consideration in evaluation of the contribution of the $I=1$ spin magnetization to the observed echo signals. The power spectrum of the experimental 90° pulse obtained from the discrete Fourier transform (FT) of the rf oscillation envelope is presented in Fig. 1, along with the power profile predicted for a "perfect-square" pulse of frequency 8.00 MHz and duration 12.5 μsec. The finite rise and fall times of the 90° pulse produce a slight narrowing in the overall power distribution.

The solid-D_2 samples were formed by condensing artificially $J=1$ enriched deuterium gas[21,22] into a Pyrex sample cell that formed an integral part of the mixing chamber of a ^{3}He-^{4}He dilution refrigerator. The temperature of the rapidly crystallized solid was monitored by a Speer carbon-resistance thermometer (220 nominal impendance, grade 1002) placed directly in the glass cell. Differential thermal-conductivity measurements[23] indicated that the ortho-para concentration of the sample quoted in this report, averaged over the conversion-induced composition changes during the experiments, was 80.0 ± 0.6% para-D_2.

III. RESULTS

Since molecular deuterium consists of two nuclear-spin species with identical gyromagnetic ratios, the NMR absorption line shape is a composite of two overlapping signals centered at an identical resonance frequency. In the cubic phase

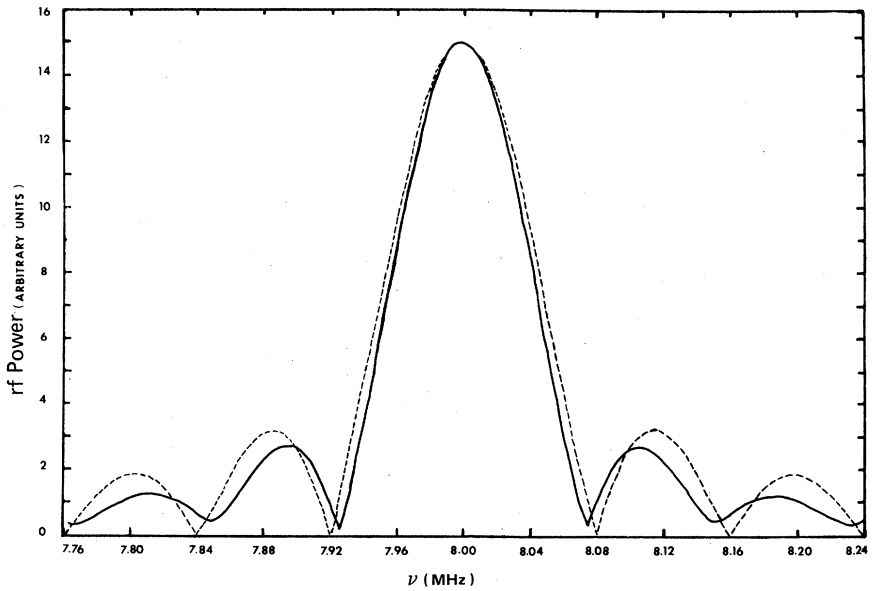

FIG. 1. Power spectrum of the experimental 90° rf pulse; (——) calculated from experimental pulse envelope; (-----) calculated for "pure-square" envelope, with $\nu_0 = 8.0$ MHz and $t_p = 12.5$ sec.

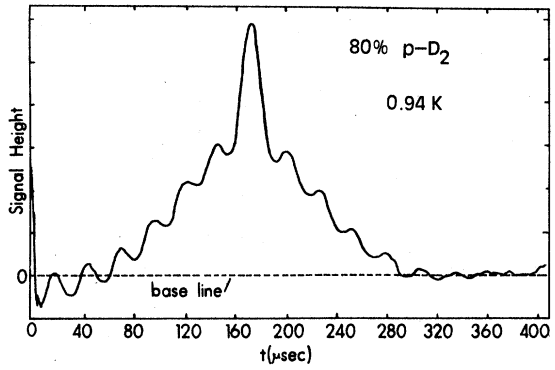

FIG. 2. Thermal-equilibrium solid-echo signal profile for 80.0% p-D_2 at 0.94 K.

the two signals are quite different in line shape; the $I=1$ signal occurring as a very broad Pake doublet about 75-kHz wide,[14] with the $I=2$ signal being much narrower, about 8-kHz wide.[14,24] Figure 2 illustrates the solid echo obtained following the standard $90°$-τ-$90°_{90°}$ pulse sequence with $\tau \sim 0.2$ msec for a thermally equilibrated sample of 80% para-D_2 at 0.94 K. For reasons of clarity the time origin is set immediately following the second $90°$ pulse. The solid-echo signal profile clearly reflects the large disparity in the absorption line shapes of the two spin systems. Superimposed on the broad smooth central component representing the narrow $I=2$ line shape, is the sharp center structure and beat pattern of the broad Pake split $I=1$ line shape for a polycrystalline specimen. The small splitting of the $I=2$ absorption that occurs at low temperatures[13,14,24] due to polarization of the $|J=0\rangle$ ground state[25] is also expected to produce a beat structure in the echo profile, but the period of these damped oscillations is approximately a factor of 10 longer than that of the $I=1$ system. The rise in signal near the end of the trace (i.e., at about $t=400$ μsec in Fig. 2 indicates the first oscillation in this small-amplitude relatively low-frequency beat pattern.

Two noteworthy features of the cubic-D_2 echo responses, both of which are clearly displayed in Fig. 2, can be attributed to the use of rf pulses in the echo sequence which did not saturate the entire $I=1$ spin system. One feature is the attenuation in the ratio of the amplitude of the sharp $I=1$ component to that of the broad $I=2$ structure, in comparison with the ratio of the total spin magnetization predicted from ortho-para composition and nuclear-spin-state degeneracies, i.e., $2x:5(1-x)$, where $x=0.80$ is the para-D_2 mole fraction. This attenuation reflects the incomplete rotation of the total $I=1$ spin system magnetization by the experimental $90°$ pulses. The other feature is the negative signal excursion and enhanced beat amplitude seen at short times t. This feature is a result of the response of the small longitudinal component of the $I=1$ magnetization remaining after the first $90°$ pulse, to the second $90°$ phase-shifted $90°_{\phi}$ pulse. A detailed explanation of the origin and interpretation of these two features is presented in Sec. IV.

IV. THEORY AND DISCUSSION

A. Theoretical interpretation of experimental measurements

In the rotationally ordered cubic phase, the $I=1$ component of the solid-D_2 NMR spectrum has a fine structure arising from the intramolecular dipole-dipole interaction.[10] The splitting $\delta\nu_{\text{intra}}$ between cusps in the line shape of a powdered sample has been shown[14,26] in the low-temperature limit to depend on the concentration x of $J=1$ of para-D_2 molecules via the relation

$$\delta\nu_{\text{intra}} = 75.25(1+0.066Z-0.021/Z)0.984 \ \text{(kHz)}, \quad (1)$$

where $Z=T_\lambda(x)/T_\lambda(x=1)$ is the ratio of the ordering temperatures of the ortho-para alloyed and pure para-D_2 solids. The spectral intensity of the unbroadened Pake line shape predicted for a particular $\delta\nu_{\text{intra}}$ will be modified by the magnetic dipolar couplings between deuterons on neighboring molecules, which give rise to a second moment contribution $\langle(\Delta\nu_{\text{intra}})^2\rangle$ approximated by[14]

$$\langle(\Delta\nu_{\text{intra}})^2\rangle = 0.031(5-3x) \ \text{(kHz}^2\text{)}. \quad (2)$$

Assuming a Gaussian distribution function for the intermolecular dipolar interactions, the intensity $\bar{P}(\nu)$ of the broadened line shape becomes[10]

$$\bar{P}(\nu) = \int_{-\infty}^{\infty} (2\pi)^{-1/2}\langle(\Delta\nu_{\text{inter}})^2\rangle^{-1/2} \times \exp\left(-\frac{(\nu-\nu_0)^2}{2\langle(\Delta\nu_{\text{inter}})^2\rangle}\right) p(\nu_0)\,d\nu_0, \quad (3)$$

where ν_0 is the frequency of the unbroadened line and $p(\nu_0)$ its intensity. Including these intermolecular dipolar effects produces a small reduction in the doublet splitting (~1%–5%) and a very slight broadening of the overall line shape. Spectra calculated for ortho-para mixtures of cubic-H_2 from relations similar to Eqs. (1)–(3) have been shown[10,12,14] to agree quantitatively with cw NMR absorption line shapes. A similar agreement for cubic-D_2 alloys is also expected, although this has yet to be explicitly demonstrated. Such agreement is not the case, however, in nearly pure ortho-H_2 or para-D_2, where anomalous features appearing

in the $I=1$ cw NMR spectra have been ascribed to a selective pumping process resulting from ortho-para conversion.[24]

Because the intermolecular dipolar couplings in cubic-D_2 are much weaker than the intramolecular interactions, it is reasonable as a first approximation to only consider the intramolecular terms in the nuclear-spin Hamiltonian when evaluating the solid-echo responses. Using this approach, we have developed a single-particle theoretical model for the $I=1$ cubic-phase echo in the case of nonrigid rotation by both pulses in the echo-creation sequence, the details of which are presented in the Appendix. The important result is that the signal $S(t)$ following the second pulse in a resonant (θ_1)-τ-$(\theta_2)_{90°}$ sequence, such as used in the present experiments, is given by

$$S(t)=2[-\cos\theta_1 \sin\theta_2 \cos\alpha(t-\tau) + i \sin\theta_1 \sin^2\theta_2 \cos\alpha(t-2\tau)], \quad (4)$$

where t is the time following application of the first pulse, θ_1 and θ_2 are the rotation angles of the respective pulses in the (θ_1)-τ-$(\theta_2)_{90°}$ echo sequence, and α is the intramolecular dipolar interaction between deuterons on a para-D_2 molecule. The first term of Eq. (4) represents the response of the longitudinal magnetization component remaining after the first pulse to the second 90° phase-shifted pulse. This term is at a maximum immediately following the second pulse, and explains the negative signal excursion and enhanced beat amplitude seen at short times after τ in the experimental echo profile given in Fig. 2. The second term describes the rephasing and subsequent dephasing of signal about $t=2\tau$ which characterizes the solid-echo envelope. Effects of nonrigid rotation for this term are governed by the two leading sinusoidal factors, which for angles <90° always produce signal attenuation. With the exception of these attenuation factors, the echo envelope is equivalent within the calculational formalism to a FID having a time of origin at $t=2\tau$.

Analysis of the mismatch between the power spectrum of the experimental 90° pulse given if Fig. 1 and the theoretical $I=1$ absorption line shape calculated from Eqs. (1)–(3) using the echo attenuation factors of Eq. (4) yields the spectral distribution of rotation angles incurred by the $I=1$ spin ensemble. Figure 3 depicts the high-frequency half of the symmetrical model line shape calculated for the total $I=1$ absorption signal from 80-at.% para-D_2 at 0.94 K, as well as the attenuated FID and solid-echo absorption signals predicted for the nonrigid rotating 90° pulses. Selective attenuation of the "wings" of the $I=1$ absorption by the narrow bandwidth of the experimental 90° pulse is clearly

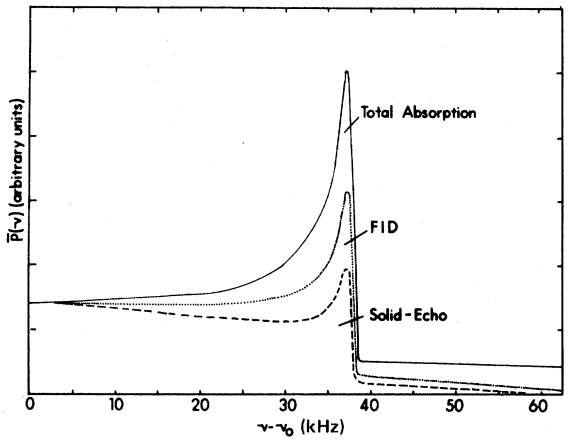

FIG. 3. Theoretical-model $I=1$ cubic-phase line shapes for 80-at.% p-D_2 at 0.94 K. (——) total absorption line shape; (· · · · ·) absorption line shape corresponding to FID signal; (-----) absorption line shape corresponding to solid-echo signal.

observable, with the sequence of pulses used in the echo case producing the largest effect. The ratio of the integrated areas of the three line shapes, 1.00 : 0.71 : 0.57, gives the relative $I=1$ spin system contribution arising in each of the three cases.

B. Comparison of theory and experiment

We have shown that in the limit of small intermolecular broadening the experimental pulse sequence produces an $I=1$ solid-echo representative of an attenuated FID with a time of origin at 2τ. Consequently, the FT of the $I=1$ echo-time profile should give rise to spectrally attenuated absorption line shape similar in form to the theoretical model line shape of Fig. 3. Figure 4 represents the pure-absorption-mode spectrum $A(\nu)$ of 80% para-D_2 at 1.4 K calculated by fast Fourier transforming (FFT) the portion of the digitized solid-echo profile starting at 2τ, using standard techniques to minimize any small residual FFT errors.[27] The calculated spectrum consists of two distinct structures: a relatively narrow, almost Gaussian structure for the $I=2$ spins, and the broad Pake split structure for the $I=1$ spins. Comparison of Fig. 4 with the published cw NMR spectrum of Maraviglia *et al.*[14] (see inset—Fig. 4) leads to the following observations: (i) the degree of attenuation of the intensity of the Pake doublet in the solid-echo spectrum is consistent with the effective rotation angle as determined from the pulse power spectrum, (ii) the splitting of the Pake doublets agree within experimental error of ±5%, and (iii) the splitting of the $I=2$ line shape is not observed in the spectrum of the echo because the low-frequency

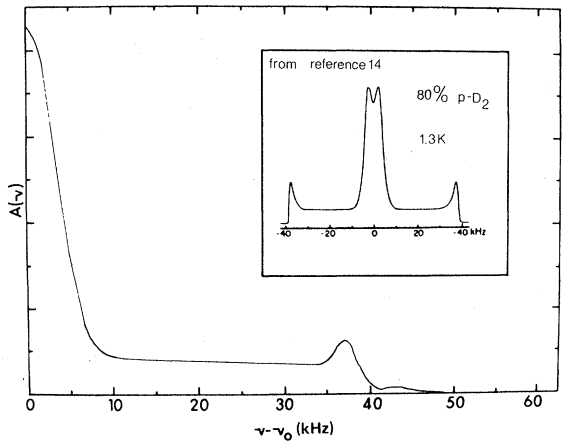

FIG. 4. Fourier transform of the solid-echo profile of thermally equilibrated 80% p-D_2 at 1.40 K (insert: cw NMR absorption line shape of 80% p-D_2 at 1.3 K from Ref. 14).

beat pattern that characterizes this splitting in the time domain was insufficiently resolved in the recorded region of echo envelope near 2τ of major interest in the present studies.

Figure 5 illustrates the fit of the theoretical model $I=1$ solid-echo line shape of Fig. 3 to the FFT of the thermally equilibrated echo profile of 80% para-D_2 at 0.94 K shown in Fig. 2. The theoretical line shape was normalized in peak height to that of the experimental spectrum. A comparative examination reveals that with the exception of a more abrupt drop in intensity on the high-frequency side of the doublet peak, the theoretical model line

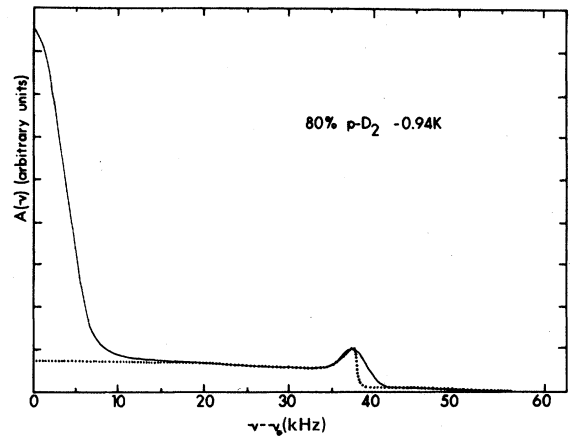

FIG. 5. Comparison of theoretical model and experimental $I=1$ line shapes for 80% p-D_2 at 0.94 K; (——) FT of equilibrium solid-echo profile; (·····) theoretical model $I=1$ solid-echo line shape given in Fig. 3.

shape and the experimental spectrum are essentially identical. In general, the fit of the two line shapes is quite good irrespective of the disparity in the falloff of the doublet peaks. This difference is also found to some extent in the cw NMR spectrum of Maraviglia *et al.*[14] shown in the insert of Fig. 4. In passing, it should be noted that a detailed analysis of distortions induced in the echo signals by the finite pickup coil and receiver bandwidths as described by Barnaal and Lowe[28] will account for at least a part of this small discrepancy.

V. SUMMARY

Nuclear-magnetic-resonance spin-echo responses in the solid hydrogens originate from effects intimately related to the molecular organization of the quantum-crystal phases. In the orientationally ordered cubic phase, the component of the local dipolar field at the $I=1$ nuclei arising from the quenched rotational motion of the $J=1$ molecules dominates these effects. The formation and shape of the $I=1$ cubic phase echo predicted solely on the basis of the contribution of the intramolecular dipolar terms of the nuclear spin Hamiltonian is found to be in remarkably good accord with the observed data.

Inherent experimental limitations in rf power associated with solid-echo measurements in cubic-phase D_2 necessitated the utilization of 90° rf pulses which did not saturate the broad $I=1$ absorption spectrum. A single-particle theoretical model for the $I=1$ solid echo in the case where nonrigid rotation is produced by both 90° pulses in the echo-creation sequence has been developed to account for selective attenuation of $I=1$ echo signal brought about by the narrow irradiative bandwidth of the experimental 90° rf pulses. The characteristic features predicted by the model have been observed in the experimental echo profiles. These are a maximum $I=1$ echo amplitude at 2τ and a subsequent signal decay that quantitatively agrees with the theoretical spectra predicted for the intramolecular dipolar interaction between $I=1$ spins on a rigid lattice when spectral attenuation due to the limited power distribution of the 90° rf pulses is taken into account. In addition, the FT of the solid-echo profile for 80% para-D_2 at 1.4 K is found to be in good agreement with the published cw NMR spectrum of Maraviglia *et al.*[14] The demonstrated ability of the intramolecular dipolar theory to accurately account for the observed echo behavior is indicative of the extent to which cooperative orientational ordering has reduced the internal dynamics of the cubic solid to that of a rigid dipolar-coupled spin system.

ACKNOWLEDGMENTS

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APPENDIX

In this Appendix we calculate the $I=1$ spin-echo response in the ordered cubic phase of solid-D_2 arising from a resonant two-pulse sequence (θ_1)-τ-$(\theta_2)_\gamma$, where τ (the time between the first pulse of rotation angle θ_1 and the second γ degree phase shifted, θ_2 degree rotation pulse) is small compared with the spin-spin relaxation time T_2. The method of calculation adopted here is based on the single-particle approach of Metzger and Gaines,[1] with the two deuteron spins on a given para-D_2 molecule treated as constituents of a single particle with spin unity whose rotating-frame Hamiltonian $\mathcal{H}'$ is approximated in the ordered cubic phase by[24,25]

$$\hbar\mathcal{H}' = \tfrac{1}{3}\delta(3\hat{J}_{\bar{z}}^2 - 2)(3\hat{I}_z^2 - 2), \tag{A1}$$

where $\bar{z}$ is the quantization axis for molecular rotation, z the nuclear spin quantization axis taken along the applied field H_0, and

$$\delta = \tfrac{3}{2}\pi d[3\cos^2(z,\bar{z}) - 1].$$

Equation (A1) ignores the intermolecular dipolar interactions of the ordered phase because they are much smaller than the intramolecular term of $\mathcal{H}'$ for the low-temperature high-percentage $J=1$ solids. It should be noted that this complete truncation of interpair terms from the spin Hamiltonian removes the deficiencies purported to arise in the single-particle formalism.[2,3]

Before application of the first rf pulse, the spin system is in thermal equilibrium at lattice temperature T, and is described by a density matrix given in the high-temperature approximation by

$$\hat{\rho}(0) \approx \exp\left(\frac{-\hbar\omega_0 I_z}{k_B T}\right) \sim 1 - \frac{\hbar\omega_0 \hat{I}_z}{k_B T}, \tag{A2}$$

where ω_0 is the Larmor frequency.

The rotation of the spin magnetization through the angle θ_1 about the y axis of the rotating frame produced by an rf pulse of duration $t_p = \theta_1/\gamma_N H_1$ (where H_1 is the rf amplitude and γ_N the gyromagnetic ratio) is described by

$$\hat{\rho}' = \exp(i\theta_1\hat{I}_y)\hat{\rho}_0\exp(-i\theta_1\hat{I}_y).$$

Regarding $3J_z^2 - 2$ as a function of time, governed by a Markov[29] process, the time evolution of the density matrix is given by

$$\hat{\rho}(t) = \exp\left(-\frac{i}{\hbar}\int_0^t \mathcal{H}'(t')\,dt'\right)\hat{\rho}(0) \times \exp\left(\frac{i}{\hbar}\int_0^t \mathcal{H}'(t')\,dt'\right). \tag{A3}$$

The signal induced in a pickup coil in the X-Y plane of the laboratory reference frame is calculated from

$$S(t) = \mathrm{Tr}[\hat{\rho}(t)\hat{I}_+], \tag{A4}$$

where Tr signifies the trace and $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$. Noting that

$$\exp(i\theta_1\hat{I}_y)\hat{I}_z\exp(-i\theta_1\hat{I}_y) = \hat{I}_z\cos\theta_1 - \hat{I}_x\sin\theta_1,$$

and that $\hat{I}_z$ commutes with $\mathcal{H}'(t')$, we obtain for the induced signal after the first pulse

$$S(t) = 2\,\mathrm{Re}\left\langle \exp i\delta\int_0^t [3\hat{J}_{\bar{z}}^2(t') - 2]\,dt'\right\rangle(-\sin\theta_1) = -2\sin\theta_1\cos\alpha t \tag{A5}$$

with $\alpha = \delta K(T)$, where the factor $K(T)$ represents the thermodynamic average of $3\hat{J}_{\bar{z}}^2 - 2$. At time $t = \tau$, the density matrix $\hat{\rho}(\tau)$ becomes

$$\hat{\rho}(\tau) = \hat{I}_z\cos\theta_1 - \sin\theta_1\exp(-i\hat{I}_z^2\alpha t)\hat{I}_x \times \exp(i\hat{I}_z^2\alpha t), \tag{A6}$$

which is consistent with the notation of Ref. 1.

We now make a rotation of the coordinates through an angle γ about the z axis and then a rotation through an angle θ_2 about the y axis, which can be simply expressed as

$$\exp(i\gamma\hat{I}_z)\hat{\rho}(\tau)\exp(-i\gamma\hat{I}_z) = \hat{I}_z\cos\theta_1 - \sin\theta_1\exp(-i\hat{I}_z^2\alpha t) \times (\hat{I}_x\cos\gamma - \hat{I}_y\sin\gamma)\exp(i\hat{I}_z^2\alpha t). \tag{A7}$$

This density matrix must now be operated on with the rotation operator[30] corresponding to the second pulse to obtain the induced signal $S(t)$. There are three terms to evaluate which we denote as (a), (b), and (c).

$$(a) = \mathrm{Tr}\{\exp[-i\alpha\hat{I}_z^2(t-\tau)]\exp(i\theta_2\hat{I}_y)\hat{I}_z\exp(-i\theta_2\hat{I}_y)\exp[i\alpha\hat{I}_z^2(t-\tau]\hat{I}_+\}\cos\theta_1\,, \tag{A8}$$

$$(b) = \mathrm{Tr}\{\exp[-i\alpha\hat{I}_z^2(t-\tau)]\exp(i\theta_2\hat{I}_y)\exp(-i\hat{I}_z^2\alpha\tau)\hat{I}_x\exp(i\hat{I}_z^2\alpha\tau) \times \exp(-i\theta_2\hat{I}_y)\exp[i\alpha\hat{I}_z^2(t-\tau)]\hat{I}_+\}(-\sin\theta_1\cos\alpha)\,, \tag{A9}$$

$$(c) = \mathrm{Tr}\{\exp[-i\alpha\hat{I}_z^2(t-\tau)]\exp(i\theta_2\hat{I}_y)\exp(-i\hat{I}_z^2\alpha\tau)\hat{I}_y\exp(i\hat{I}_z^2\alpha\tau) \times \exp(-i\theta_2\hat{I}_y)\exp[i\alpha\hat{I}_z^2(t-\tau)]\hat{I}_+\}(\sin\theta_1\sin\gamma)\,. \tag{A10}$$

First we examine term (a) vis the development of Eq. (A5) and find that

$$(a) = -\cos\theta_1\sin\theta_2\,2\cos\alpha(t-\tau)\,. \tag{A11}$$

Next, for the term (b), we explicitly write the sums over m, m_1, m_2, and m_3 using the fact that

$$\langle m_1|\exp(-i\hat{I}_z^2\tau)\hat{I}_x\exp(i\alpha\hat{I}_z^2\tau)|m\rangle = \exp[i\alpha(m^2-m_1^2)\tau]\langle m_1|\hat{I}_x|m\rangle\,.$$

$$(b) = \sum_{m,m_1,m_2,m_3}\langle m|\exp(i\theta_2\hat{I}_y)|m_1\rangle\exp[i\alpha(m_2^2-m_1^2)\tau]\langle m_1|\hat{I}_x|m_2\rangle\langle m_2|\exp(-i\theta_2\hat{I}_y)|m_3\rangle \times \exp[i\alpha(t-\tau)(m_3^2-m^2)]\langle m_3|\hat{I}_+|m\rangle\,. \tag{A12}$$

Also, since

$$\langle m_1|\hat{I}_x|m_2\rangle = \tfrac{1}{2}\{[2-m_2(m_2+1)]^{1/2}\delta_{m_1,m_2+1} + [2-m_2(m_2-1)]^{1/2}\delta_{m_1,m_2-1}\}\,,$$

Eq. (A12) is factorable into terms that, after summing over m_1 and m_3 to utilize the δ functions, with the remaining sums being taken explicitly, are of the general form

$$(b) = \frac{1}{2}\sum_m \sqrt{2}\,\langle m|\exp(i\theta_2\hat{I}_y)|\sigma\rangle\exp(-iK\theta_2\hat{I}_y)\langle\sigma'|\exp(-i\theta_2\hat{I}_y)|m+1\rangle \times \exp[i\alpha(t-\tau)(2m+1)][2-m(m+1)]^{1/2}\,, \tag{A13}$$

where the factors σ, K, and σ' take the values $(1,0,0,-1)$, $(-1,1,1,-1)$, and $(0,-1,1,0)$, respectively. Substitution of the explicit forms for the rotation matrices[30] yields the following simplified form for term (b):

$$(b) = 2\cos\theta_2\cos\alpha t(-\sin\theta_2\cos\gamma)\,. \tag{A14}$$

The evaluation of term (c) is carried out similarly to (b), with the final result expressed by

$$(c) = 2i[\cos^2\theta_2\cos\alpha t + \sin^2\theta_2\cos\alpha(t-2\tau)]\sin\theta_2\sin\gamma\,. \tag{A15}$$

Collecting terms (a), (b), and (c), the general expression for the signal following the second pulse becomes

$$S(t) = 2[-\cos\theta_1\sin\theta_2\cos\alpha(t-\tau) - \cos\gamma\sin\theta_1\cos\theta_2\cos\alpha t + i\cos^2\theta_2\sin\theta_1\sin\gamma\cos\alpha t + i\sin\gamma\sin\theta_1\sin^2\theta_2\cos\alpha(t-2\tau)]\,. \tag{A16}$$

Finally, for the experimental conditions where $\gamma = 90°$ and τ is of the order of T_2,

$$[S(t)]_{\gamma=90°,\,\tau\sim T_2} \approx 2[-\cos\theta_1\sin\theta_2\cos\alpha(t-\tau) + i\sin\theta_1\sin^2\theta_2\cos\alpha(t-2\tau)]\,, \tag{A17}$$

which is the desired result.

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