

NMR Spin Echoes for Molecular Rotators with C_3 Symmetry

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NMR spin echoes are calculated for a rotator consisting of three spin- $\frac{1}{2}$ nuclei whose three-particle wave function obeys C_3 symmetry. On decomposing the nuclear dipole-dipole interactions in terms of irreducible operators of the representations of the group C_3 it is found that for spins belonging to the A-representation, the echo amplitude is maximized for a $\frac{\pi}{2}$ - π RF pulse sequence. The dependences of the echo formation on the orientation of the rotor and on the strengths of the dipolar interactions and the magnetic field inhomogeneities are discussed. © 2000 Academic Press

Key Words: dipolar interactions; molecular symmetry; C_3 symmetry; rotators.

1. INTRODUCTION

NMR spin-echo techniques at high magnetic fields where the internuclear dipole-dipole interactions are only a small perturbation on the nuclear Zeeman energy can be used to distinguish between different molecular symmetry states. While these symmetry properties have been exploited to determine the absorption spectra for NMR and NQR applications (1–6), the potential of developing special RF pulse sequences to provide unique signatures of the underlying group symmetries has not been fully explored. This capability is well-known for proton pairs in solid hydrogen (7) for which the ortho molecules (total nuclear spin $I = 1$, orbital angular momentum $J = 1$) have echo sequences that are distinctly different from those formed by independent spin- $\frac{1}{2}$ pairs if the ortho molecules have a preferred orientation. Similar results were observed for solid D_2 for which the molecular species are ortho ($J = 0$, $I = 2$, 0) and para ($J = 1$, $I = 1$) (8). Use has been made also of group symmetry properties for calculations of NMR relaxation rates (9–11) and for the off-resonance responses of quadrupolar nuclei (12) and multiquantum spectra of multispin systems (13, 14). The purpose of this paper is to show that molecular systems of more complex symmetries, and in particular the three-spin rotors, have special NMR echo responses that reflect the symmetry states. For the ortho-hydrogen molecule this echo behavior is best demonstrated by treating the intramolecular dipole-dipole interaction in terms of irreducible operators in the manifold $I = 1$, $J = 1$, and we follow a similar approach in this paper.

Motivated by the search for a special RF pulse technique that could be used to demonstrate directly the multispin cyclic permutation of particle exchange in solid ^3He (15, 16), we have calculated the conditions for NMR spin-echo formation for a coupled assembly of three spin- $\frac{1}{2}$ nuclei whose rotational state obeys C_3 symmetry. This result would be expected to apply to some methyl and ammonium rotator groups as well as to the three-spin exchange operator for ^3He atoms on a triangular lattice. Unusual NMR echoes with maxima for $\frac{\pi}{2}$ - π RF pulse sequences were reported for NMR studies of methyl groups in $(\text{TMTSF})_2\text{X}$ by Hanson (17) and this result can be understood in terms of the underlying symmetry properties of the dipolar interactions for the rotator states. A similar feature has been explored by Man *et al.* (18) for single spin systems with quadrupolar nuclei. In order to be applicable the lifetime of the relevant molecular symmetry state must be longer than the nuclear spin relaxation time. While this is true for the symmetry species of simple molecules (H_2 , D_2 , CH_4 . . .) and low-dimensional molecular chains such as $(\text{TMTSF})_2\text{X}$, it will not be valid for short-lived states in some methyl and ammonia groups (19). In the following sections we first show how to express the intramolecular interactions in terms of irreducible operators and then calculate the NMR spin echoes for a $\frac{\pi}{2}$ - β pulse sequence (where β is variable) for two cases: (i) intramolecular dipolar interactions only and (ii) magnetic field homogeneities plus dipolar interactions.

2. NUCLEAR DIPOLE-DIPOLE INTERACTIONS

We calculate the formation of NMR spin echoes for a molecule with three spin- $\frac{1}{2}$ nuclei, I_s (for $s = 1, 2, 3$), whose internuclear axes r_{st} form a planar rotator with C_3 symmetry. We consider only the case of high magnetic fields for which the nuclear Zeeman interaction $\mathcal{H}_Z = -\gamma\hbar \sum_i I_{iz} B_z$ is large compared to the dipolar interactions. In this case we need only retain the secular part of the dipolar interactions, i.e., the part that commutes with I_z where the applied magnetic field is parallel to the z -axis. For each pair of spins (st) the dipolar interaction is given by (20)

$$\mathcal{H}_{\text{DD}}^{st} = -\sqrt{\frac{24\pi}{5}} D \sum_{\mu} [\sum_{m,n} C_{mn,\mu}^{112} I_m^s I_n^t Y_{\mu}^2(\theta^{(st)}, \phi^{(st)})], \quad [1]$$

where μ , m , and n refer to the vectorial components $I_0 = I_z$, $I_{\pm 1} = \mp 2^{-1/2}(I_x \pm I_y)$, and C_{mn}^{112} is a Clebsch–Gordan coefficient. $Y_{\mu}^2(\theta^{(st)}, \phi^{(st)})$ is the spherical harmonic for the polar angles $(\theta^{(st)}, \phi^{(st)})$ defining the orientation of the internuclear axis $r_{(st)}$ with respect to the local molecular reference frame. The strength of the dipolar interaction for an internuclear separation r_0 is given by $D = \gamma^2 \hbar^2 / r_0^3$. The total dipolar interaction $\mathcal{H}_{\text{DD}}^T = \sum_{(st)} \mathcal{H}_{\text{DD}}^{st}$ where the sum is over all independent pairs (st) of the nuclear spins.

In order to exploit the symmetry properties of the rotational variables for the values of $(\theta, \phi)_{(st)}$ which are correlated, we need to rewrite $\mathcal{H}_{\text{DD}}^T$ in terms of operators that transform irreducibly according to the representations of the group C_3 . We therefore need nuclear spin functions that are simultaneous eigenfunctions of the operators \mathcal{F}_z , \mathcal{F}^2 , and \mathcal{P}_s where \mathcal{F} is the total nuclear spin, and \mathcal{P}_s is the spin permutation operator. In terms of the nuclear spin eigenfunctions $|m_1 m_2 m_3\rangle$ (where m_s is the eigenvalue of I_z^s), the required orthonormal linear combinations are given by (5, 6)

$$\begin{aligned} & |m_1 m_2 m_3; A^{(1)}\rangle \\ &= \frac{1}{\sqrt{3}} (|m_1 m_2 m_3\rangle + |m_2 m_3 m_1\rangle + |m_3 m_1 m_2\rangle) \\ & |m_1 m_2 m_3; E^a\rangle \\ &= \frac{1}{\sqrt{3}} (|m_1 m_2 m_3\rangle + \epsilon |m_2 m_3 m_1\rangle + \epsilon^* |m_3 m_1 m_2\rangle) \\ & |m_1 m_2 m_3; E^b\rangle \\ &= \frac{1}{\sqrt{3}} (|m_1 m_2 m_3\rangle + \epsilon^* |m_2 m_3 m_1\rangle + \epsilon |m_3 m_1 m_2\rangle), \quad [2] \end{aligned}$$

where $\epsilon = e^{2\pi i/3}$. The wave functions that depend on the spatial coordinates are classified in terms of eigenfunctions of the permutation group \mathcal{P}_m of the three masses, i.e., $\mathcal{P}_m |n; A^{(2)}\rangle = |n; A^{(2)}\rangle$, $\mathcal{P}_m |n; E^a\rangle = \epsilon |n; E^a\rangle$, and $\mathcal{P}_m |n; E^b\rangle = \epsilon^* |n; E^b\rangle$, where $n = 0$ corresponds to the molecular ground state. $|0; E^a\rangle$ and $|0; E^b\rangle$ are degenerate but separated from $|0; A^{(2)}\rangle$ by the tunneling energy splitting $\hbar J$.

The complete wavefunction for the three fermions must be totally antisymmetric, and the only allowed combinations of space and nuclear spin functions are therefore those whose product contains the representation $A^{(2)}$, i.e.,

$$\begin{aligned} \Phi_1 &= |0; A^{(2)}\rangle |m_1 m_2 m_3; A^{(1)}\rangle \\ \Phi_2 &= |0; E^a\rangle |m_1 m_2 m_3; E^b\rangle \\ \Phi_3 &= |0; E^b\rangle |m_1 m_2 m_3; E^a\rangle. \end{aligned} \quad [3]$$

Following the notation developed by Nijman (21) for the tetrahedral group, we can write

$$\mathcal{H}_{\text{DD}}^T = -\sqrt{6} D \sum_{\Gamma, \zeta} \sum_{\mu} (-)^{\mu} \mathcal{B}_{2,-\mu}^{\Gamma, \zeta} \mathcal{G}_{2, \mu}^{\Gamma, \zeta}. \quad [4]$$

(Γ, ζ) label the irreducible representations ($A^{(1)}$, E^a , E^b). $\mathcal{G}_{2\mu}^{\Gamma, \zeta}$ is the spherical component of a three-spin nuclear spin operator that transforms irreducibly according to the representation (Γ, ζ) , and

$$\mathcal{B}_{2m}^{\Gamma, \zeta}(\mathcal{M}) = \sum_{(st)} \mathcal{A}_{st}^{\Gamma, \zeta} \mathcal{B}_{2m}^{\Gamma, \zeta}, \quad [5]$$

where for each pair of nuclei (st)

$$\mathcal{B}_{2m}^{(st)} = \sqrt{\frac{4\pi}{5}} Y_m^2(\theta^{st}, \phi^{st}). \quad [6]$$

If the nuclear sites are labeled (1, 2, 3), the normalized matrix elements of $\mathcal{A}_{st}^{\Gamma, \zeta}$ are given by

$$\mathcal{A}_{st}^{\Gamma, \zeta} = \begin{matrix} x^2 + y^2, z^2; A^1 \\ x^2 - y^2, xy; E^a \\ xz, yz; E^b \end{matrix} \begin{pmatrix} (12) & (23) & (31) \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} & \epsilon & \epsilon^* \\ \frac{1}{\sqrt{3}} & \epsilon^* & \epsilon \end{pmatrix}. \quad [7]$$

We have included with the labels (Γ, ζ) the basis functions for the different representations. A useful review of multipole operators has been given by Sanctuary (22).

Keeping only the secular component, $\mu = 0$, the intramolecular dipolar interaction that dephases the transverse nuclear magnetization following an initial $\frac{\pi}{2}$ pulse is given by

$$\mathcal{H}_{\text{DD}_0}^T = -\sqrt{6} D \sum_{\Gamma, \zeta} \mathcal{B}_{20}^{\Gamma, \zeta} \mathcal{G}_{20}^{\Gamma, \zeta}, \quad [8]$$

with the quantization axis Z parallel to the applied magnetic field. This quantization axis does not in general coincide with one of the symmetry axes for the molecular rotator, and we need to further decompose $\mathcal{B}_{20}^{\Gamma, \zeta}$ into the rotator basis functions for the local molecular frame of reference. This decomposition is achieved with a rotation by the polar angles (Θ, Φ) which

specify the orientation of the magnetic field with respect to the threefold symmetry axes of the molecule and the plane of the molecule. This leads to

$$\mathcal{H}_{\text{DD}_0}^T = -\sqrt{6}D \sum_{\Gamma, \zeta} \sum_m \mathcal{B}_{2m}^{\Gamma, \zeta}(\mathcal{M}) Y_m^2(\Theta, \Phi) \mathcal{F}_{20}^{\Gamma, \zeta}, \quad [9]$$

where the $\mathcal{B}_{2m}^{\Gamma, \zeta}(\mathcal{M})$ transform irreducibly in the molecular frame of reference, \mathcal{M} .

We calculate the $\mathcal{B}_{2m}^{\Gamma, \zeta}(\mathcal{M})$ in the standard molecular frame of reference with the z -axis parallel to the threefold axis of rotation and the x -axis aligned parallel to the vector \mathbf{r}_1 . In this reference frame $\theta_{(12)} = \theta_{(23)} = \theta_{(31)} = \frac{\pi}{2}$, $\phi_{(12)} = \frac{5\pi}{6}$, $\phi_{(23)} = \frac{3\pi}{2}$, and $\phi_{(31)} = \frac{13\pi}{6}$. Direct calculation for the molecular reference frame (\mathcal{M}) yields

$$\mathcal{B}_{2, \mu}^{\Gamma, \zeta}(\mathcal{M}) = \mu: \begin{matrix} E^a \\ E^b \end{matrix} \begin{pmatrix} -2 & -1 & 0 & 1 & 2 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{3}{\sqrt{8}} \\ \frac{3}{\sqrt{8}} & 0 & 0 & 0 & 0 \end{pmatrix}. \quad [10]$$

For the components of $\mathcal{H}_{\text{DD}_0}$ that transform according to the A-representation, we find for the laboratory frame of reference, $\mathcal{B}_{20}^{A1}(\mathcal{L}) = -(\sqrt{3}/2)D(3 \cos^2\Theta - 1)$, and

$$\mathcal{H}_{\text{DD}_0}^{A1} = \frac{3D}{2\sqrt{2}} (3 \cos^2\Theta - 1) \mathcal{F}_{20}^{A1}, \quad [11]$$

with $\mathcal{F}_{20}^{A1} = [(\mathcal{F}_z^{\text{Tot}})^2 - \frac{1}{3}(\mathcal{F}^{\text{Tot}})^2]$. The total effective nuclear spin \mathcal{F}^{Tot} is a spin- $\frac{3}{2}$ operator for the A-representation. We will show in the next section that the dependence on a higher order tensorial component results in a very different spin-echo sequence compared to that for uncorrelated fermions. The matrix elements are $\langle A_{3/2}^{(1)} | \mathcal{H}_{\text{DD}_0}^{A1} | A_{3/2}^{(1)} \rangle = \frac{3}{2}D(3 \cos^2\Theta - 1)$ and $\langle A_{1/2}^{(1)} | \mathcal{H}_{\text{DD}_0}^{A1} | A_{1/2}^{(1)} \rangle = -\frac{3}{2}D(3 \cos^2\Theta - 1)$. $\mathcal{H}_{\text{DD}_0}^{A1}$ is a maximum for $\Theta = \frac{\pi}{2}$ (i.e., for magnetic fields aligned parallel to the plane of the rotator) and vanishes for magnetic fields lying on the surface of the cone defined by the magic angle $\cos^{-1}(1/\sqrt{3})$ with respect to the threefold axis of rotation.

The E-representation has total effective nuclear spin $\mathcal{F}^{\text{Tot}} = \frac{1}{2}$. The dipolar interactions therefore have the same symmetry properties as independent spin- $\frac{1}{2}$ particles for the E-components of the intramolecular dipole–dipole interaction, and they contribute a standard spin echo sequence. The two E-components of $\mathcal{H}_{\text{DD}_0}$ have a strong dependence on the orientation of the magnetic field. $\mathcal{H}_{\text{DD}_0}^{Ea} = -\sqrt{6}\mathcal{B}_{2,0}^{Ea}\mathcal{F}_{2,0}^{Ea}$ and $\mathcal{H}_{\text{DD}_0}^{Eb} = -\sqrt{6}\mathcal{B}_{2,0}^{Eb}\mathcal{F}_{2,0}^{Eb}$ with $\mathcal{B}_{2,0}^{Ea} = (\mathcal{B}_{2,0}^{Eb})^* = (3\sqrt{3}/8)D \sin^2\Theta e^{2i\Phi}$. There are off-diagonal elements of the nuclear spin operators between the E^a and E^b representations, with $\langle E^b | \mathcal{H}_{\text{DD}_0}^{Ea} | E^a \rangle =$

$D\alpha$ and $\langle E^b | \mathcal{H}_{\text{DD}_0}^{Eb} | E^a \rangle = D\alpha^*$. The eigenstates of the E-components of the dipolar interactions are therefore given by $(|E^a\rangle \pm |E^b\rangle)\sqrt{2}$, with eigenvalues $\pm|\alpha| = \pm\frac{3}{8}D \sin^2\Theta_m$. The E-component of the intramolecular dipole–dipole interaction is a maximum for $\Theta = \frac{\pi}{2}$ independent of Φ , i.e., for an applied magnetic field aligned parallel to the plane of the rotator. For $\Theta = 0$ and the applied field parallel to the axis of symmetry, these dipolar contributions vanish.

3. CALCULATION OF NUCLEAR SPIN ECHOES

We calculate the NMR spin-echo amplitude for a $\frac{\pi}{2}$ - t - β RF pulse sequence for which an initial pulse rotates the spins about the y -axis by $\frac{\pi}{2}$ and creates a transverse nuclear magnetization I_x in the rotating frame (20). After a time t a second pulse rotates the spins by an angle β about an axis in the x - y plane that makes an angle ψ with the y -axis. The time dependence of the magnetization is determined by the total perturbing Hamiltonian,

$$\mathcal{H}_{\text{pert}} = \sum_i \Delta_i I_{zi} + 2\hbar J \sum_{st} I_s \cdot I_t + \mathcal{H}_{\text{DD}_0}^{\text{Tot}}, \quad [12]$$

where $\Delta_i = \gamma\hbar\Delta B_i$ are the perturbations due to local magnetic field inhomogeneities (ΔB_i) and J is the exchange rate for the permutation of particles (s, t).

At time t the nuclear spin density matrix in the rotating frame is

$$\rho(t) = e^{-i\mathcal{H}_{\text{pert}}t} I_x e^{i\mathcal{H}_{\text{pert}}t} \quad [13]$$

and the echo amplitude at time t' after the second pulse is

$$\begin{aligned} E(t, t') &= \text{Tr}[e^{-i\mathcal{H}_{\text{pert}}t'} \mathcal{R} \rho(t) \mathcal{R}^\dagger e^{i\mathcal{H}_{\text{pert}}t'} I_x] \\ &= \text{Tr}[\mathcal{R} \rho(t) \mathcal{R}^\dagger \rho(-t')], \end{aligned} \quad [14]$$

where \mathcal{R} is the rotation operator for the second pulse.

The significant feature of the system under study is that the dominant perturbing interactions are described in terms of simple single spin operators that transform irreducibly under the symmetry operations of the molecular symmetry group. The time dependence and the echo amplitudes can be calculated in a straightforward manner using the operators $\mathcal{F}_{mn}^{\Gamma, \zeta}$. For the E-representation, we showed in the previous section that $\mathcal{H}_{\text{DD}_0}^E$ leads to conventional echo formation and we therefore only consider terms belonging to the symmetrical A-representation.

In order to carry out the calculations we need to transform the Cartesian operator I_x into components of the orthonormal spherical operators \mathcal{F}_m^1 obeying the orthogonality relations $\text{Tr}[\mathcal{F}_m^l \mathcal{F}_{m'}^{l'}] = \delta_{mm'}(-^m)$. Following the standard convention (23) for $l = 1$, we use the spherical components $\mathcal{F}_0^1 = I_z$, $\mathcal{F}_{\pm 1}^1$

$= \mp(2)^{-1/2}\mathbf{I}_{\pm 1}^1$. In the manifold of the E-representation ($\mathcal{F}^{\text{Tot}} = \frac{3}{2}$), the matrix representations $\langle m|\mathcal{F}_n^1|m'\rangle$ are

$$\mathcal{F}_1^1 = -\frac{1}{\sqrt{10}} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad [15]$$

and

$$\mathcal{F}_0^1 = \frac{1}{\sqrt{5}} \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}, \quad [16]$$

with $\mathcal{F}_{-1}^1 = (-)(\mathcal{F}_1^1)^\dagger$.

The initial density matrix,

$$\rho(0) = I_x = -\frac{1}{\sqrt{2}} (\mathcal{F}_1^1 - \mathcal{F}_{-1}^1), \quad [17]$$

and $\rho(t)$ can be calculated in terms of the $\mathcal{F}_m^l(t)$ using the A-representation expression $\mathcal{H}_{\text{DDO}}^{\rho A1} = \mathcal{D}\mathcal{F}_0^2 = \mathcal{D}[(\mathcal{F}_z^{\text{Tot}})^2 - \frac{1}{3}(\mathcal{F}^{\text{Tot}})^2]$ where $\mathcal{D} = D(3 \cos^2\Theta - 1)$.

Including the local field inhomogeneities ΔI_z ,

$$\mathcal{F}_1^1(t) = -\frac{1}{\sqrt{10}} e^{-i\Delta t} \begin{pmatrix} 0 & \sqrt{3}e^{-2i\mathcal{D}t} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3}e^{2i\mathcal{D}t} \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad [18]$$

The time-dependent operator can now be simply decomposed into a linear sum of time-independent operators \mathcal{F}_m^l .

$$\begin{aligned} \mathcal{F}_1^1(t) = & -\frac{1}{\sqrt{10}} e^{-i\Delta t} \left[\sqrt{\frac{3}{5}} \cos 2\mathcal{D}t (2\mathcal{F}_1^3 + \sqrt{6}\mathcal{F}_1^1) \right. \\ & \left. + \sqrt{\frac{2}{5}} (2\mathcal{F}_1^1 - \sqrt{6}\mathcal{F}_1^3) - \sqrt{6}i \sin 2\mathcal{D}t \mathcal{F}_1^2 \right] \end{aligned} \quad [19]$$

and $\mathcal{F}_{-1}^1(t) = -\mathcal{F}_1^1(t)^\dagger$.

The effect of the second rotation $\mathcal{R}(\beta, \psi)$ is now trivial to calculate, because for the irreducible spherical operators \mathcal{F}_m^l ,

$$\mathcal{R}\mathcal{F}_m^l\mathcal{R}^\dagger = e^{-im\psi} \sum_{\mu} d_{m\mu}^l \mathcal{F}_{\mu}^l, \quad [20]$$

where $d_{m\mu}^l$ are the matrix elements of the rotation matrix operator. Using a repeated suffix notation,

$$\begin{aligned} \mathcal{R}\mathcal{F}_{\pm 1}^1\mathcal{R}^\dagger & = -\frac{1}{\sqrt{50}} e^{\mp i\Delta t} \left[\sqrt{3} \cos(2\mathcal{D}t) (2d_{\pm 1m}^3 \mathcal{F}_m^3 + \sqrt{6}d_{\pm 1m}^1 \mathcal{F}_m^1) \right. \\ & \quad \left. + 2(\sqrt{2}d_{\pm 1m}^1 \mathcal{F}_m^1 - \sqrt{3}d_{\pm 1m}^3 \mathcal{F}_m^3) \right. \\ & \quad \left. \mp i\sqrt{30} \sin(2\mathcal{D}t) d_{\pm 1m}^2 \mathcal{F}_m^2 \right], \end{aligned} \quad [21]$$

from which we can calculate $\mathcal{R}\rho(t)\mathcal{R}^\dagger$ in Eq. [14].

Using the expression for $\rho(-t')$ and the orthogonality relations, we find for the NMR spin echo amplitude,

$$\begin{aligned} E(t, t') = & -\frac{1}{100} \cos(\Delta(t-t')) [6 \cos(2\mathcal{D}t) \cos(2\mathcal{D}t') \\ & \quad \times (4d_{-11}^3 + 6d_{-11}^1) + 8(2d_{-11}^1 + 3d_{-11}^3) \\ & \quad + 60 \sin(2\mathcal{D}t) \sin(2\mathcal{D}t') d_{-11}^2 \\ & \quad + 24(\cos(2\mathcal{D}t) + \cos(2\mathcal{D}t')) (d_{-11}^1 - d_{-11}^3)] \\ & + \frac{1}{100} \cos(\Delta(t+t')) \cos(2\psi) \\ & \quad \times [6 \cos(2\mathcal{D}t) \cos(2\mathcal{D}t') \\ & \quad \times (4d_{11}^3 + 6d_{11}^1) + 8(2d_{11}^1 + 3d_{11}^3) \\ & \quad - 60 \sin(2\mathcal{D}t) \sin(2\mathcal{D}t') d_{11}^2 + 24(\cos(2\mathcal{D}t) \\ & \quad + \cos(2\mathcal{D}t')) (d_{11}^1 - d_{11}^3)]. \end{aligned} \quad [22]$$

If the magnetic field inhomogeneities are significant then only the first term in Eq. [22] contributes to the echo at time $t = t'$. The echo amplitude for $\Delta = 0$ is

$$\epsilon_{(1)}^{\Delta \neq 0}(t = t') = -\frac{1}{50} (17d_{-11}^1 + 15d_{-11}^2 + 18d_{-11}^3). \quad [23]$$

Using the expressions for the elements of the rotation matrices, we find

$$\begin{aligned} \epsilon_{(1)}^{\Delta \neq 0}(t = t') & = -\frac{1}{160} (38 - 5 \cos \beta - 6 \cos 2\beta - 27 \cos 3\beta). \end{aligned} \quad [24]$$

The term in $\cos 3\beta$ results in a strong contribution to the echo for $\beta = \frac{\pi}{3}$ and the variation of the total amplitude of the echo as a function of β is shown in Fig. 1. If the phase angle $\psi = 0$ or π the echo amplitude is negative for all values of β . Two equally strong minima occur at $\beta = 64.2^\circ$ and 180° . As a check

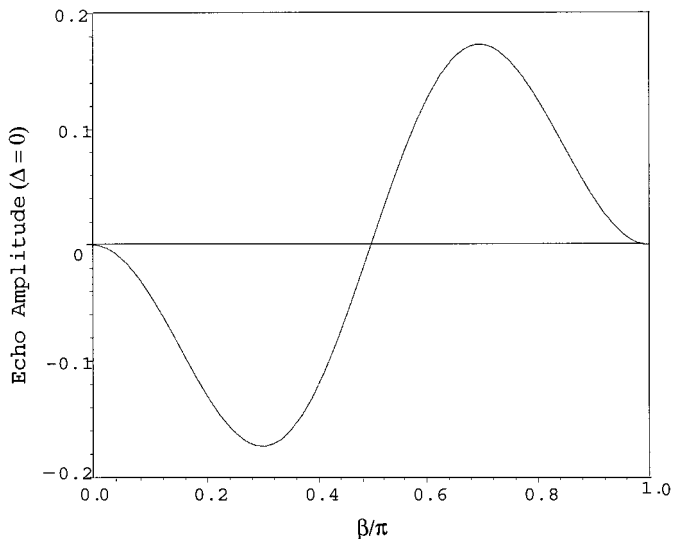


FIG. 1. Variation of the NMR spin-echo amplitude for a C_3 rotator in an inhomogeneous magnetic field as a function of β for a $\frac{\pi}{2}$ - β RF pulse sequence. This variation includes the time-independent terms of Eq. [22]. (The echo amplitudes are normalized to unity for the free induction decay signal.)

on the calculations we note that if we put $\mathcal{D} = 0$, the echo amplitude $\mathcal{E}^{\Delta \neq 0}(t = t') = -d_{-11}^1 = -\frac{1}{2}(1 - \cos \beta)$ and is maximum negative for $\beta = \pi$ as expected for a conventional echo sequence. It is worth noting that the echo amplitude given by Eq. [22] contains a time-independent term that also varies with β . If we consider only the time-dependent terms, the echo amplitude is given by

$$\epsilon_{(2)}^{\Delta \neq 0}(t = t') = -\frac{9}{160} (2 + \cos \beta - 2 \cos 2\beta - \cos 3\beta). \quad [25]$$

The dependence of this component of the echo on β is shown in Fig. 2 and has a strong negative peak at $\beta = \cos^{-1}(\sqrt{\frac{2}{3}}) = 70.5^\circ$. The case $t = t' = 0$ is a special case because the term $(\cos 2\mathcal{D}t + \cos 2\mathcal{D}t')$ in Eq. [2] now contributes to the echo amplitude which becomes $\mathcal{E}^{\Delta \neq 0}(t = t' = 0) = -\frac{1}{25}(19d_{-11}^1 + 6d_{-11}^3) = -1$ for $\beta = 0$.

If we can neglect the field inhomogeneities, i.e., if $|\Delta t| \ll 1$ for typical values of t , e.g., $t = T_2$, then the second term in Eq. [22] also contributes to the echo, and we have for $\psi = 0$ or π

$$\begin{aligned} \epsilon_{(3)}^{\Delta=0, \psi=0}(t = t') &= \frac{3}{100} [6(d_{11}^1 - d_{-11}^1) - 10(d_{11}^2 + d_{-11}^2) \\ &\quad + 4(d_{11}^3 - d_{-11}^3)] \\ &= -\frac{9}{80} (\cos \beta - \cos 3\beta). \end{aligned} \quad [26]$$

As shown in Fig. 3, this echo (for $\psi = 0$) has a minimum for $\beta_m = \cos^{-1}(1/\sqrt{3}) = 54.7^\circ$ and a maximum at $\beta = \pi - \beta_m$, with equal amplitudes for both extrema. For $\psi = \frac{\pi}{2}$, i.e., a $(\frac{\pi}{2})_y - (\beta)_x$ RF pulse sequence,

$$\epsilon_{(4)}^{\Delta=0, \psi=\pi/2}(t = t') = -\frac{9}{40} (1 - \cos 2\beta). \quad [27]$$

For this sequence the echo is maximum and negative for $\beta = \frac{\pi}{2}$, corresponding to the familiar *solid* echo for dipolar interactions.

4. DISCUSSION AND CONCLUSION

The calculated amplitudes of the echo formation for a general $\frac{\pi}{2}$ - β pulse sequence for a molecule of three spin- $\frac{1}{2}$ nuclei whose rotational wavefunction obeys C_3 symmetry have unique features. For an oriented system with the magnetic field aligned parallel to the plane of the rotators, the NMR spin-echo amplitude is a maximum for $\beta \approx \frac{\pi}{3}$. For a homogeneous magnetic field, the maximum echo amplitude occurs for $\beta = 54.7^\circ$, and for inhomogeneous magnetic fields, the maximum occurs for $\beta = 64.2^\circ$. This feature can be used to identify the rotational symmetry, provided that the exchange frequency J which determines the energy separation of the states satisfies $J > \mathcal{D}$. If $J < \mathcal{D}$, the above analysis is not valid and the system behaves as independent fermions.

It is important to note that the rotational (or exchange) frequency J does not enter directly into the expression for the NMR echo formation. The exchange spin operator is diagonal in the A- and the E-representations and therefore does not

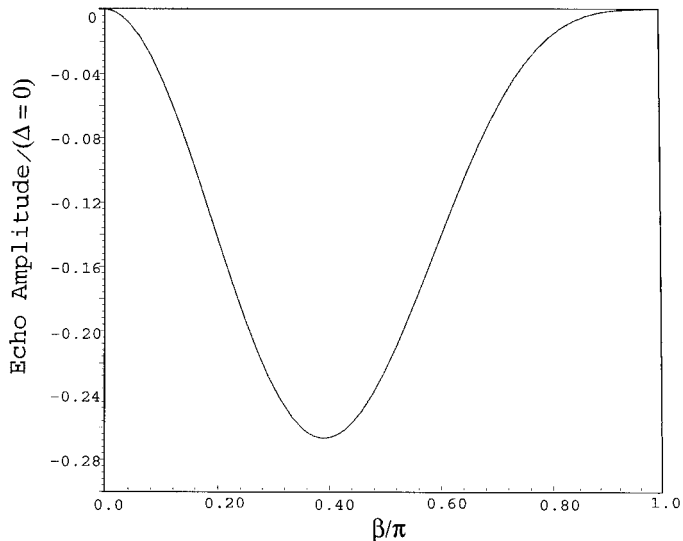


FIG. 2. Variation of the time-dependent components only of the NMR spin-echo amplitude for a C_3 rotator in an inhomogeneous magnetic field as a function of β for a $\frac{\pi}{2}$ - β RF pulse sequence. (The echo amplitudes are normalized to unity for the free induction decay signal.)

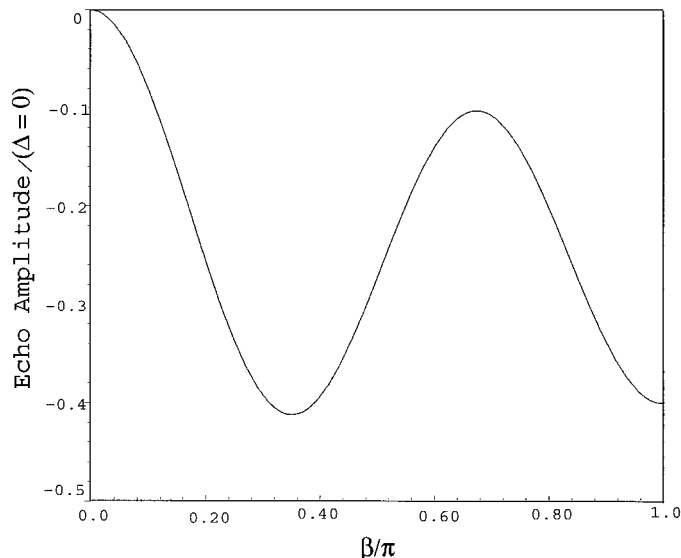


FIG. 3. Variation of the NMR spin-echo amplitude for a C₃ rotator in a homogeneous magnetic field as a function of β for a $\frac{\pi}{2}$ - β RF pulse sequence. (The echo amplitudes are normalized to unity for the free induction decay signal.)

contribute directly to the temperature dependence. If there were an appreciable mixing of the A- and E-wavefunctions, this would not be true because the matrix elements $\langle A | \mathcal{J}'_m(t) | E \rangle$ would be permitted with a resulting time dependence $\exp[iJ(t - t')]$ for the echo amplitude. In the absence of such a mixing, NMR measurements cannot measure J directly. The exchange frequency can, however, be inferred from NMR relaxation studies because, as a result of the modulation of the intermolecular dipolar interactions, the spectral densities of the motions that determine the relaxation are sharply peaked at J . This feature has been used for bulk samples of ³He (24).

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