Formation of echo signals in aligned (but unpolarized) quadrupole spin systems

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Echo signals are computed in a three-level quadrupolar spin system ($I=1$) with small or almost zero asymmetry parameter, where the ground (equilibrium) state is determined not by a polarization vector but by an alignment tensor. Transformation supermatrices express the action of pulses and internal interactions. The evolution of the system is presented in the form of a graph, showing the trajectories for transfer of coherence and magnetization. It is shown that the echo signal is less than the free precession signal amplitude by not more than a factor of two. The formalism predicts the formation of an echo signal near or at zero frequency.

1. INTRODUCTION

We have observed previously an irreversible attenuation of transverse magnetization in a quadrupole spin system with an axially symmetric electric field gradient (EFG) tensor.[1,2] Numerical calculations[2] showed that homonuclear dipole–dipole interactions, usually considered responsible for this attenuation, are too weak in such compounds to explain the experimental results. Moreover, it was shown experimentally that deuteration of a specimen resulted in an appreciable increase (by more than an order of magnitude) in the lifetime of transverse magnetization.[2]

These experiments stimulated a detailed theoretical discussion of the possibility of formation of echo signals in three-level quadrupolar spin systems with a pair of degenerate, or close to degenerate levels. In this case the ground state Hamiltonian is defined as an alignment tensor and not a polarization vector (using Blum's terminology[3]).

A quadrupolar three-level system with zero symmetry parameter was studied earlier[4] with approximations allowing the problem to be reduced to a consideration of a two-level system. In the present work it is assumed that because of the spread in the components of the EFG tensor the same shift of both two-level transition frequencies takes place. We assume that as a consequence of this spread there is an arbitrary shift in each energy level, which leads both to a shift of mean frequency and to the appearance of a normally distributed asymmetry parameter with zero mean value. In addition, we consider systems with small (nonzero) asymmetry parameter in order to obtain the dependence of the parameters of the transition signals on changes in the asymmetry parameter.

In presenting the material we first consider the features of the Hamiltonians of internal interactions in systems with asymmetry parameter η close to zero in relation to systems with large[5] and zero[4] value. These properties will determine new features in the evolution of the spin system.

2. INTERACTION HAMILTONIAN

For $I=1$, the quadrupole interaction Hamiltonian

$$\mathcal{H}_Q=K[3I_z^2-\eta(I_x^2-I_y^2)]$$

can be written with the help of fictitious spin-1/2 operators (Ref. 6) (single-transition operators according to the terminology of Ernst *et al.*[7]) in the form

$$\mathcal{H}_Q=\omega_p S_z^p+\tfrac{1}{3}(\omega_q-\omega_r)(S_z^q-S_z^r), \tag{1}$$

where $K=e^2qQ/4$ is the quadrupole interaction constant, the indices p, q, and r indicate transitions between levels $+\leftrightarrow 0$, $0\leftrightarrow -$ and $-\leftrightarrow +$ ($E_+=K(1+\eta)$, $E_-=K(1-\eta)$, $E_0=-2K\eta$). Determination of the transition operators and the commutation relation are given in Appendix 1. The three transition frequencies $\omega_p=K(3+\eta)$, $\omega_q=-K(3-\eta)$ and $\omega_r=-2K\eta$ satisfy the condition $\omega_p+\omega_q+\omega_r=0$, which, when taking account of the property $S_z^q+S_z^p+S_z^r=0$ of the single-transition operators, allows us to write the quadrupolar Hamiltonian of Eq. (1) in three equivalent forms by means of cyclic permutation of the indices. All the S_z operators commute with one another, which under the condition $S_z^q+S_z^p+S_z^r=0$ corresponds to the existence of two integrals of the motion determined by the operators S_z^p and $S_z^q-S_z^r$, which can be considered the polarization vector and the alignment tensor.[3]

Because of the symmetry of Eq. (1) under permutation of the indices, such a separation is possible by three equivalent means relative to each transition frequency. If the three transition frequencies differ appreciably from one another, then the frequency of an external radio-frequency field can coincide with only one of them, ω_p, and only produces transitions between that pair of levels. All the operators (S_z^p, S_y^p, and S_x^p) of this transition commute with the operator $S_z^q-S_z^r$, so that a vector model of a two-level system can be used to describe the processes of formation of a spin echo. If the asymmetry parameter is close to zero, then one of the transition frequencies, $\omega_r=-2K\eta$, also becomes close to zero, the alignment tensor becomes a ground-state Hamiltonian, and transverse magnetization is excited in all three transitions, which considerably complicates the description of echo signal formation.

The interaction Hamiltonian of the spin system with a radio-frequency magnetic field

$$\mathcal{H}_1'=\gamma H_1(c_xI_x+c_yI_y+c_zI_z)\cos(\omega t+\phi)$$

can be written with the help of single-transition operators as

$$\mathcal{H}_1'=2\sum_{m=p}^{r}\omega_1^m S_x^m\cos(\omega t+\phi), \tag{2}$$

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where H_1, ω, and ϕ are the amplitude, frequency and phase of the radio-frequency field, c_x, c_y, c_z are the direction cosines of the r.f. field vector in the system of the principal axes of the EFG tensor, $\omega_1^m=\gamma H_1 c_m$ is the nutation frequency, and γ is the gyromagnetic ratio. In the interaction picture

$$\begin{aligned}\mathcal{H}_1&=\exp(i\mathcal{H}_Q t)\mathcal{H}_1' \exp(-i\mathcal{H}_Q t)\\&=\sum_{m=p}^{r} \omega_1^m\{S_x^m[\cos(\omega_m-\omega)t-\phi]\\&\quad -S_y^m[\sin(\omega_m-\omega)t-\phi]\}.\end{aligned} \tag{3}$$

If the frequency of the external field coincides with the frequency of one transition, then upon neglecting rapidly oscillating terms, we can obtain

$$\mathcal{H}_1=\sum_{m=p}^{r} \omega_1^m[S_x^m \cos\phi+S_y^m \sin\phi]. \tag{4}$$

The initial phase of the first pulse can be set equal to zero and the phases of subsequent pulses can be counted from it. Then

$$\mathcal{H}_1=\omega_1^m S_x^m . \tag{5}$$

This case is realized for large asymmetry parameters.

For zero asymmetry parameter, the frequency of the external field coincides (at resonance) with the frequencies of two transitions and

$$\mathcal{H}_1=\omega_1^p S_x^p+\omega_1^q S_x^q=\omega_1(c_x S_x^p+c_y S_x^q).$$

In this case the positions of the principal x and y axes are undefined, and with no loss of generality we can put $c_y=0$, which again leads to Eq. (5). However, the coordinate system is now determined by the projection of the r.f. field vector, and because of the asymmetry of the EFG tensor, the operator responsible for the splitting of the levels is non-diagonal in this coordinate system.

Hamiltonian of heteronuclear dipole–dipole interactions. These interactions can be considered interactions of a spin system with a local magnetic field $\mathbf{H_L}$, and the expression for the Hamiltonian is the same as Eq. (2) if we omit the $\cos(\omega t+\phi)$ and replace ω_1 by ω_L

$$\mathcal{H}_{IS}=\sum_{m=p}^{r} \omega_L^m S_x^m . \tag{6}$$

In the interaction picture,

$$\mathcal{H}_{IS}=\sum_{m=p}^{r} \omega_L^m[S_x^m \cos(\omega_m t)-S_y^m \sin(\omega_m t)]. \tag{7}$$

In the case of nonzero asymmetry parameter this Hamiltonian does not contain constant terms, and consequently only makes a contribution to broadening in second-order perturbation theory. If $\eta=0$ then ω_r is also equal to zero, and

$$\mathcal{H}_{IS}=\omega_L^r S_x^r . \tag{8}$$

The Hamiltonian of inhomogeneous broadening. For small asymmetry parameter, the basic Hamiltonian, which is determined by the alignment tensor, can be written in the form

$$\mathcal{H}_Q=\tfrac{2}{3}\omega_Q(S_z^p-S_z^q), \tag{9}$$

where $\omega_Q=(E_+ + E_- -2E_0)/2=3K$ is the mean quadrupole resonance frequency. Consequently the Hamiltonian of inhomogeneous broadening—i.e., of the frequency shift—can be represented as

$$\mathcal{H}_\Delta=\tfrac{2}{3}\Delta(S_z^p-S_z^q), \tag{10}$$

where $\Delta=\omega_Q-\omega$.

It is also necessary to take into account the level-splitting Hamiltonian

$$\mathcal{H}_\delta=\omega_r S_x^r=-2K\eta S_z^r . \tag{11}$$

In a coordinate system in which the x axis is directed along the r.f. field vector, the position of the x and y axes of the spin operator $\mathbf{I}$ is determined by the rotation operator I_z or, equivalently, by the operator S_x^r.

Consequently

$$\mathcal{H}_\delta'=\omega_r(S_z^r \cos 2\alpha+S_y^r \sin 2\alpha), \tag{12}$$

where α is the angle between the principal x axis of the EFG tensor and the projection of the r.f. field vector on the xy plane.

In this way, the evolution of the spin system in the interval between the pulses will take place under the action of two commuting Hamiltonians: the Hamiltonian of the shift $\mathcal{H}_\Delta$, and the total Hamiltonian for splitting and heteronuclear dipole interactions.

$$\begin{aligned}\mathcal{H}_r&=\mathcal{H}_\delta'+\mathcal{H}_{IS}=\omega_L S_x^r+\omega_r S_z^r \cos 2\alpha+\omega_r S_y^r \sin 2\alpha\\&=\omega_e(n_x S_x^r+n_y S_y^r+n_z S_z^r)=\omega_e(\mathbf{n}\mathbf{S}^r),\end{aligned} \tag{13}$$

where

$$n_s=\frac{\omega_L}{\omega_e},\quad n_y=\frac{\omega_r \sin 2\alpha}{\omega_e},\quad n_z=\frac{\omega_r \cos 2\alpha}{\omega_e}$$

are the direction cosines of the effective field, and $\omega_e=\sqrt{\omega_r^2+\omega_L^2}$ is the effective spin precession frequency in "r" subspace.

We proceed now to a calculation of the transition signals in the spin system.

3. CALCULATION OF TRANSITION SIGNALS

The initial density matrix determined by the Hamiltonian of Eq. (9) is given by

$$\rho_0=\tfrac{2}{3}(S_z^p-S_z^q), \tag{14}$$

where we omit the unit operator and a constant factor for the calculations.

To find an expression for the density matrix describing the formation of an echo, it is necessary to carry out a sequence of transformations of the initial density matrix, corresponding to the action of the first pulse, the evolution of

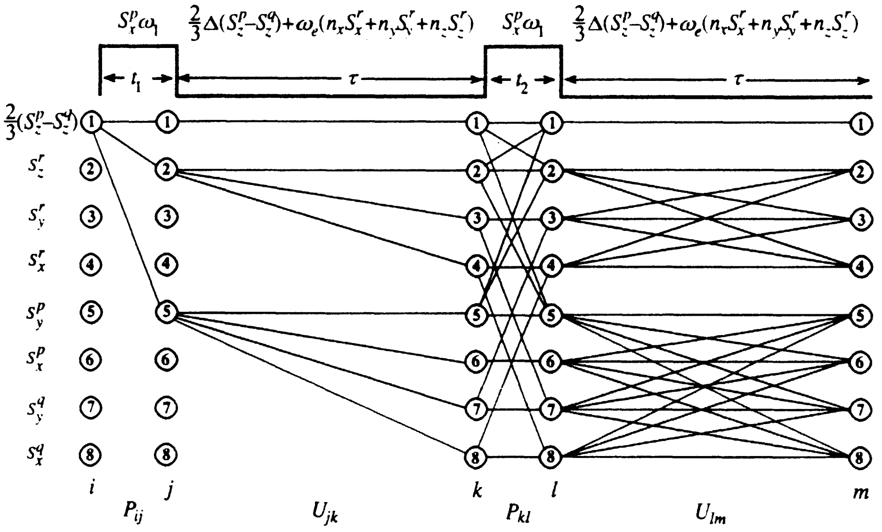

FIG. 1. Trajectories of the evolution of a spin system during formation of echo signals. Elements of the **P** and **U** matrices are shown in Appendices 2 and 3.

free precession under the action of the Hamiltonians of Eqs. (10) and (13) and the second pulse, and subsequent free precession evolution:

$$\begin{aligned}\rho_1=&\exp[-i(\mathcal{H}_\Delta+\mathcal{H}_r)t]\exp[-i\omega_1S_x^pt_2]\\&\times\exp[-i(\mathcal{H}_\Delta+\mathcal{H}_r)\tau]\\&\times\exp[-i\omega_1S_x^pt_1]\rho_0\\&\times\exp[i\omega_1S_x^pt_1]\exp[i(\mathcal{H}_\Delta+\mathcal{H}_r)\tau]\\&\times\exp[i\omega_1S_x^pt_2]\exp[i(\mathcal{H}_\Delta+\mathcal{H}_r)t]\\=&\sum_{\substack{\beta=x,y,z\\m=p,q,r}}a_\beta^mS_\beta^m.\end{aligned}\tag{15}$$

The action of a pulse can be expressed in terms of one-transition operators, using the propagator $\exp(i\psi S_x^p)$. These transformations are well known, and for reference are given in Appendix 2. The operators $\mathcal{H}_\Delta$ and $\mathcal{H}_r$ commute, so they can be considered to act in succession. Furthermore, $\mathcal{H}_\Delta$ commutes with all operators of the subspace "r," and the transformation in this subspace is a conventional three-dimensional rotation by an angle ω_et around the axis determined by the direction cosines n_x, n_y, n_z:

$$\begin{aligned}&\exp[-i\omega_et(\mathbf{nS}^r)]\mathbf{S}^r\exp[+i\omega_et(\mathbf{nS}^r)]\\&\quad=(\mathbf{nS}^r)\mathbf{n}+[\mathbf{n}[\mathbf{nS}^r]]\cos(\omega_et)\\&\qquad+[\mathbf{nS}^r]\sin(\omega_et).\end{aligned}\tag{16}$$

The transformations in the two other subspaces can in general be represented by

$$\begin{aligned}&\exp[-i\omega_et(\mathbf{nS}^r)]S_{x,y}^{r,q}\exp[+i\omega_et(\mathbf{nS}^r)]\\&\quad=S_{x,y}^{p,q}\cos\left(\frac{\omega_et}{2}\right)-i[\mathbf{nS}^r,S_{x,y}^{p,q}]\sin\left(\frac{\omega_et}{2}\right).\end{aligned}\tag{17}$$

The general transformation matrix corresponding to the period of evolution is shown in Appendix 3. It is of block-diagonal form, and separates into vector and tensor subspaces.

Using the transformation rules given in the Appendices, the general expression for the solution of Eq. (15) can be written down. However, it would be too complicated for presentation. We therefore express our results in the form of a graph and follow the evolution of the spin system along the trajectories shown in Fig. 1.

As can be seen from Fig. 1, a radio-frequency pulse in the "p" subspace produces a transfer of coherence from "r" subspace to "q" subspace and back, while the vector (r) and tensor (pq) subsystems evolve independently of one another. Since what is observed in the present case is transverse magnetization corresponding to the operator S_y^p, it is necessary for us to consider the evolution of the system along the trajectories

1. $S_z^p-S_z^q\xrightarrow{P_{1.5}}S_y^p\xrightarrow{U_{5.5}}S_y^p\xrightarrow{P_{5.5}}S_y^p\xrightarrow{U_{5.5}}S_y^p$,

2. $S_z^p-S_z^q\xrightarrow{P_{1.5}}S_y^p\xrightarrow{U_{5.6}}S_x^p\xrightarrow{P_{6.6}}S_x^p\xrightarrow{U_{6.5}}S_y^p$,

3. $S_z^p-S_z^q\xrightarrow{P_{1.5}}S_y^p\xrightarrow{U_{5.7}}S_y^q\xrightarrow{P_{7.7}}S_y^q\xrightarrow{U_{7.5}}S_y^p$,

4. $S_z^p-S_z^q\xrightarrow{P_{1.5}}S_y^p\xrightarrow{U_{5.8}}S_x^q\xrightarrow{P_{8.8}}S_x^q\xrightarrow{U_{8.5}}S_y^p$.

The "classical" (vector) echo is produced along trajectories 1 and 2. The corresponding contributions to the density matrix can be written by using transformation matrices **P** and **U**:

$$a_y^{P(1)}=P_{1.5}U_{5,5}P_{5.5}U_{5.5}$$
$$=\frac{1}{4}\sin\psi_1\left(2\cos^2\frac{\psi_2}{2}-1\right)\Big\{(1+n_z^2)$$
$$\times\left[\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\cos(\Delta(t+\tau))\right.$$
$$\left.+\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\cos(\Delta(t-\tau))\right]+(1-n_z^2)$$
$$\times\left[\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\cos(\Delta(t-\tau))\right.$$
$$\left.+\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\cos(\Delta(t+\tau))\right]$$
$$+2n_z\left[\sin\left(\frac{\omega_e}{2}(t+\tau)\right)\sin(\Delta(t+\tau))\right.$$
$$\left.\left.+\sin\left(\frac{\omega_e}{2}(t-\tau)\right)\sin(\Delta(t-\tau))\right]\right\}, \quad (18)$$

$$a_y^{P(2)}=P_{1.5}U_{5.6}P_{6.6}U_{6.5}$$
$$=\frac{1}{4}\sin\psi_1\Big\{(1+n_z^2)\left[\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\cos\Delta((t+\tau))\right.$$
$$\left.-\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\cos(\Delta((t-\tau))\right]+(1-n_z^2)$$
$$\times\left[-\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\cos(\Delta(t-\tau))\right.$$
$$\left.+\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\cos(\Delta(t+\tau))\right]$$
$$+2n_z\left[\sin\left(\frac{\omega_e}{2}(t+\tau)\right)\sin(\Delta(t+\tau))\right.$$
$$\left.\left.-\sin\left(\frac{\omega_e}{2}(t-\tau)\right)\sin(\Delta(t-\tau))\right]\right\}. \quad (19)$$

As usual, terms describing approaching isochromats at $t=\tau$ (time is reckoned from the second pulse) $\cos[(\omega_e/2)(t-\tau)]\cos[\Delta(t-\tau)]$ correspond to the echo signals. The product $\cos[(\omega_e/2)(t+\tau)]\cos[\Delta(t+\tau)]$ represents the free precession signal after the first pulse. Terms representing converging isochromats with frequencies $\omega_e/2$ and diverging ones with frequencies Δ, and vice versa, also appear in Eqs. (18) and (19), due to the existence of we commuting mismatch operators.

The complete result of evolution along trajectories 1 and 2 gives the expression

$$a_y^{P(1,2)}=\frac{1}{2}\sin\psi_1\left\{\left[(1+n_z^2)\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\right.\right.$$
$$\left.+(1-n_z^2)\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\right]\cos(\Delta(t+\tau))$$
$$\left.+2n_z\sin\left(\frac{\omega_e}{2}(t+\tau)\right)\sin(\Delta(t+\tau))\right\}\cos^2\frac{\psi_2}{2}$$
$$-\frac{1}{2}\sin\psi_1\left\{\left[(1+n_z^2)\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\right.\right.$$
$$\left.+(1-n_z^2)\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\right]\cos(\Delta(t-\tau))$$
$$\left.+2n_z\sin\left(\frac{\omega_e}{2}(t-\tau)\right)\sin(\Delta(t-\tau))\right\}\sin^2\frac{\psi_2}{2}, \quad (20)$$

from which it can be seen that the maximum value of the echo signal in this case is

$$\frac{1}{2}(1+n_z^2)\sin\psi_1\sin^2\frac{\psi_2}{2} \quad (21)$$

and can only reach the same magnitude as the free precession signal when $n_z=1$. This occurs when the local field vanishes ($\omega_L=0$) and the principal x axis of the EFG tensor points in the direction of the r.f. field vector.

The result for the evolution along trajectories 3 and 4,

$$a_y^{P(3,4)}=P_{1.5}U_{5.7}P_{7.7}U_{7.5}+P_{1.5}U_{5.8}P_{8.8}U_{8.5}$$
$$=\frac{1}{4}\sin\psi_1\cos\frac{\psi_2}{2}\Big\{-[(n_x^2-n_y^2)(\cos\Delta(t-\tau))$$
$$+(n_x^2+n_y^2)\cos(\Delta(t+\tau))+n_xn_y\sin(\Delta(t$$
$$-\tau))]\left[\cos\left(\frac{\omega_e}{2}(t-\tau)\right)-\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\right]$$
$$+[(n_x^2-n_y^2)\cos(\Delta(t-\tau))-(n_x^2+n_y^2)$$
$$\times\cos(\Delta(t+\tau))+n_xn_y\sin(\Delta(t-\tau))]$$
$$\times\left[\cos\left(\frac{\omega_e}{2}(t-\tau)\right)-\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\right]$$
$$=\frac{1}{2}\sin\psi_1\cos\frac{\psi_2}{2}(1-n_z^2)\left[\cos\left(\frac{\omega_e}{2}(t+\tau)\right)\right.$$
$$\left.-\cos\left(\frac{\omega_e}{2}(t-\tau)\right)\right]\cos(\Delta(t+\tau)) \quad (22)$$

shows that an echo signal of opposite polarity is produced along each trajectory, and these cancel. In order for them to add, it is necessary to apply a pulse in q subspace, i.e., to use crossed coils. Another feature of the evolution along trajectories 3 and 4 is the combination of isochromats at frequencies ω_e, which would be suppressed by a frequency offset Δ.

Analogous contributions to the observed signal come from evolution along the trajectories:

$$5.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.3}} S_y^r \xrightarrow{P_{3.7}} S_y^q \xrightarrow{U_{7.5}} S_y^p,$$

$$6.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.4}} S_x^r \xrightarrow{P_{4.8}} S_x^q \xrightarrow{U_{8.5}} S_y^p,$$

$$7.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.2}} S_z^r \xrightarrow{P_{2.5}} S_y^p \xrightarrow{U_{5.5}} S_y^p$$

$$a_y^{p(5,6)} = \frac{1}{2}\sin^2\frac{\psi_1}{2}\sin\frac{\psi_2}{2}(1-n_z^2)\left[\cos\left(\omega_e\left(\frac{t}{2}-\tau\right)\right) - \cos\left(\omega_e\left(\frac{t}{2}+\tau\right)\right)\right]\cos\Delta t,$$

$$a_y^{p(7)} = \sin^2\frac{\psi_1}{2}\sin^2\psi_2(1-n_z^2)\left[\cos\left(\omega_e\left(\frac{t}{2}-\tau\right)\right) + \cos\left(\omega_e\left(\frac{t}{2}+\tau\right)\right)\right]\cos(\Delta t). \quad (23)$$

One feature of these signals is their appearance 2τ after the second pulse, since the isochromats diverge in "r" subspace with frequency ω_e, while they approach in "pq" subspace at half that frequency. Both signals are attenuated because of the spread in Δ, and can only be observed if the spread in Δ is appreciably less than that in ω_e.

The process of magnetization transfer in "r" subspace and the formation of the echo signal in it can also be represented clearly in Fig. 1. Consider the evolution along trajectories

$$8.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.2}} S_z^r \xrightarrow{P_{2.2}} S_z^r \xrightarrow{U_{2.2}} S_z^r,$$

$$9.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.3}} S_y^r \xrightarrow{P_{3.3}} S_y^r \xrightarrow{U_{3.2}} S_z^r,$$

$$10.\quad S_z^p - S_z^q \xrightarrow{P_{1.2}} S_z^r \xrightarrow{U_{2.4}} S_x^r \xrightarrow{P_{4.4}} S_x^r \xrightarrow{U_{4.2}} S_z^r.$$

The density matrix describing the evolution along these trajectories contains a term corresponding to the echo signal:

$$a_z^{r(8,9,10)} = \sin^2\frac{\psi_1}{2}\sin^4\frac{\psi_2}{2}(1-n_z^2)^2\cos[\omega_e(t-\tau)]. \quad (24)$$

Since the operator $S_z^p - S_z^q$ commutes with all operators of the r subspace, the spread of frequencies Δ does not appear during formation of the echo (Eq. 24). This signal is only observable after the third (90°) pulse. The first pulse must be a 180° pulse and the second pulse a 360° pulse. Such a sequence of pulses is somewhat reminiscent of Jeener and Broekaert's experiment.[8] In essence it also involves transfer of magnetization to an unobservable reservoir with subsequent use of a "revealed" pulse.

Our method can also be used to calculate the stimulated echo. It is sufficient for this to consider evolution along the trajectory

$$11.\quad S_z^p - S_z^q \xrightarrow{P_{15}} S_y^p \xrightarrow{U_{55}} S_y^p \xrightarrow{P_{51}} S_z^p - S_z^q \xrightarrow{U_{11}} S_z^p - S_z^q \xrightarrow{P_{15}} S_y^p,$$

$$a_y^{p(11)} = \frac{9}{16}\sin\psi_1\sin\psi_2\sin\psi_3\left\{(1+n_z^2)\left[\cos\frac{\omega_e}{2}(t-\tau)\times\cos\Delta(t-\tau) + \cos\frac{\omega_e}{2}(t+\tau)\cos\Delta(t+\tau)\right] + (1-n_z^2)\left[\cos\frac{\omega_e}{2}(t-\tau)\cos\Delta(t+\tau) + \cos\frac{\omega_e}{2}(t+\tau)\cos\Delta(t-\tau)\right]\right\}.$$

In this case an echo signal is produced, as well as free precession signals proportional to $(1+n_z^2)$, plus signals determined by the reduction in the spread of frequencies ω_e in the free precession signal background and in the spread of frequencies Δ and vice versa, which are proportional to $(1-n_z^2)$. All three should be 90° pulses.

4. CONCLUSIONS

The conditions for the formation of an echo signal in systems with initial state described by an alignment tensor are considered for the example of NQR of ^{14}N. The free evolution (in the absence of a pulse) proceeds independently in the two subspaces (vector and tensor). Radio-frequency pulses produce a transfer of coherence from one subspace to the other. In a three-level system with three transition frequencies, inhomogeneous broadening is characterized by two independent quantities, conveniently expressed by a displacement (shift) of the mean frequency and splitting of the levels. Evolution in the vector subspace is only determined by the splitting, while in the tensor subspace it is determined by the splitting and the shift. The transfer of coherence leads to a phase advance confined to one subspace, uncompensated in the other subspace. As a result, echo signals corresponding to convergence of the isochromats is formed with a spread, for example, of splittings against an attenuation background with a frequency spread, and vice versa. For these reasons, two-stage attenuation of the echo signal is possible relative to the free precession signal.

A radio-frequency pulse produces polarization in the vector space, which makes it possible to observe an echo signal at zero carrier frequency.

It is convenient to analyze multilevel systems with the aid of a graph, with which one can trace the evolution of the system along different trajectories corresponding to the transfer of coherence between different pairs of levels.

The authors hope that the calculations carried out above can also be useful in other areas of spectroscopy where the echo signal technique is used, for example in nonlinear optics.

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APPENDIX 1. DEFINITIONS OF FICTITIOUS SPIN-1/2 OPERATORS AND COMMUTATION RELATIONS BETWEEN THEM.

$$S_x^p=\tfrac{1}{2}I_x,\quad S_y^p=\tfrac{1}{2}(I_yI_z+I_zI_y),\quad S_z^p=\tfrac{1}{2}(I_z^2-I_y^2),$$

$$S_x^q=\tfrac{1}{2}I_y,\quad S_y^q=\tfrac{1}{2}(I_xI_z+I_zI_x),\quad S_z^q=\tfrac{1}{2}(I_x^2-I_z^2),$$

$$S_x^r=\tfrac{1}{2}I_z,\quad S_y^r=\tfrac{1}{2}(I_yI_x+I_xI_x),\quad S_z^r=\tfrac{1}{2}(I_y^2-I_x^2),$$

$$[S_x^p,S_x^q]=-[S_y^p,S_y^q]=\tfrac{1}{2}iS_x^r,\quad [S_x^p,S_y^q]=[S_y^p,S_x^q]=\tfrac{1}{2}iS_y^r,$$

$$[S_x^p,S_z^q]=[S_y^p,S_z^r]=\tfrac{1}{2}iS_y^p,\quad [S_a^m,S_b^m]=\tfrac{1}{2}iS_c^m\ (m=p,\ q,\ r\ \text{and}\ a,\ b,\ c=x,\ y,\ z\ \text{plus cyclic permutations}).$$

APPENDIX 2. SUPERMATRIX OF TRANSFORMATIONS CORRESPONDING TO THE ACTION OF A RADIO-FREQUENCY PULSE.

Operators	$\frac{1}{\sqrt{3}}(S_z^p-S_z^q)$	S_z^r	S_y^r	S_x^r	S_y^p	S_x^p	S_y^q	S_x^q
$\frac{1}{\sqrt{3}}(S_z^p-S_z^q)$	$\frac{1}{4}(1+3\cos\psi)$	$\frac{\sqrt{3}}{2}\sin^2\frac{\psi}{2}$	0	0	$\frac{\sqrt{3}}{2}\sin\psi$	0	0	0
S_z^r	$\frac{\sqrt{3}}{2}\sin^2\frac{\psi}{2}$	$\frac{1}{4}(3+\cos\psi)$	0	0	$-\frac{1}{2}\sin\psi$	0	0	0
S_y^r	0	0	$\cos\frac{\psi}{2}$	0	0	0	$-\sin\frac{\psi}{2}$	0
S_x^r	0	0	0	$\cos\frac{\psi}{2}$	0	0	0	$\sin\frac{\psi}{2}$
S_y^p	$-\frac{\sqrt{3}}{2}\sin\psi$	$\frac{1}{2}\sin\psi$	0	0	$\cos\psi$	0	0	0
S_x^p	0	0	0	0	0	1	0	0
S_y^q	0	0	$\sin\frac{\psi}{2}$	0	0	0	$\cos\frac{\psi}{2}$	0
S_x^q	0	0	0	$-\sin\frac{\psi}{2}$	0	0	0	$\cos\frac{\psi}{2}$

APPENDIX 3. SUPERMATRIX OF TRANSFORMATIONS CORRESPONDING TO A PERIOD OF FREE EVOLUTION.

Operators	$\frac{(S_z^p-S_z^q)}{\sqrt{3}}$	S_z^r	S_y^r	S_x^r	S_y^p	S_x^p	S_y^q	S_x^q
$\frac{(S_z^p-S_z^q)}{\sqrt{3}}$	1							
S_z^r		$2n_z^2\sin^2\frac{\omega_c t}{2}+$ $+\cos\omega_e t$	$2n_yn_z\sin^2\frac{\omega_c t}{2}-$ $-n_x\sin\omega_e t$	$2n_yn_z\sin^2\frac{\omega_c t}{2}+$ $+n_y\sin\omega_e t$				
S_y^r		$2n_yn_z\sin^2\frac{\omega_c t}{2}+$ $+n_x\sin\omega_e t$	$2n_y^2\sin^2\frac{\omega_c t}{2}+$ $+\cos\omega_e t$	$2n_xn_y\sin^2\frac{\omega_c t}{2}-$ $-n_z\sin\omega_e t$				
S_x^r		$2n_yn_z\sin^2\frac{\omega_c t}{2}+$ $+n_y\sin\omega_e t$	$2n_xn_y\sin^2\frac{\omega_c t}{2}+$ $+n_z\sin\omega_e t$	$2n_x^2\sin^2\frac{\omega_c t}{2}+$ $+\cos\omega_e t$				
S_y^p					$\cos\frac{\omega_c t}{2}\cos\Delta t+$ $+n_z\sin\frac{\omega_c t}{2}\sin\Delta t$	$-\cos\frac{\omega_c t}{2}\sin\Delta t+$ $+n_z\sin\frac{\omega_c t}{2}\cos\Delta t$	$-\big(n_x\cos\Delta t-$ $-n_y\sin\Delta t\big)\sin\frac{\omega_c t}{2}$	$-\big(n_x\sin\Delta t+$ $+n_y\cos\Delta t\big)\sin\frac{\omega_c t}{2}$
S_x^p					$\cos\frac{\omega_c t}{2}\sin\Delta t-$ $-n_z\sin\frac{\omega_c t}{2}\cos\Delta t$	$\cos\frac{\omega_c t}{2}\cos\Delta t$ $-n_z\sin\frac{\omega_c t}{2}\sin\Delta t$	$-\big(n_x\sin\Delta t+$ $+n_y\cos\Delta t\big)\sin\frac{\omega_c t}{2}$	$\big(n_x\cos\Delta t-$ $-n_y\sin\Delta t\big)\sin\frac{\omega_c t}{2}$
S_y^q					$\big(n_x\cos\Delta t+$ $+n_y\sin\Delta t\big)\sin\frac{\omega_c t}{2}$	$\big(-n_x\sin\Delta t+$ $+n_y\cos\Delta t\big)\sin\frac{\omega_c t}{2}$	$\cos\frac{\omega_c t}{2}\cos\Delta t-$ $-n_z\sin\frac{\omega_c t}{2}\sin\Delta t$	$\cos\frac{\omega_c t}{2}\sin\Delta t+$ $\pm n_z\sin\frac{\omega_c t}{2}\cos\Delta t$
S_x^q					$\big(-n_x\sin\Delta t+$ $+n_y\cos\Delta t\big)\sin\frac{\omega_c t}{2}$	$-\big(n_x\cos\Delta t-$ $-n_y\sin\Delta t\big)\sin\frac{\omega_c t}{2}$	$-\cos\frac{\omega_c t}{2}\sin\Delta t-$ $-n_z\sin\frac{\omega_c t}{2}\cos\Delta t$	$\cos\frac{\omega_c t}{2}\cos\Delta t-$ $-n_z\sin\frac{\omega_c t}{2}\sin\Delta t$

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