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Relaxation due to thermal vibrations in pulsed EPR: Cylindrical-fluctuation model of perturbation of $\tilde{g}$- and $\tilde{A}$-matrices of an electron-nuclear spin-coupled system in a malonic-acid single crystal

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In the context of pulsed electron paramagnetic resonance (EPR), the correlation time (τ_c) and an effective parameter, representing the fluctuation of the director of the malonic-acid molecule due to thermal motion in the directions transverse to the molecular symmetry axis, are calculated. These calculations are made using the experimental electronic and nuclear spin relaxation times of an electron-nuclear spin-coupled system (electron spin $S = 1/2$; nuclear spin $I = 1/2$), as determined from echo electron-electron double-resonance (echo-ELDOR) measurements in a γ-irradiated malonic acid single crystal for a specific orientation of the external magnetic field with respect to the crystal axes. To this end, thermal motion of the molecule is considered to cause fluctuations in the values of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$ (hyperfine) matrices of the spin system, which are calculated using the model of Frezzato *et al.* [J. Phys. Chem. B, **108**, 9505 (2004)] as functions of the thermal motion of the malonic-acid molecule in the directions transverse to its symmetry-axis. These fluctuations, i.e. the time-dependent variation from the average values of the spin-Hamiltonian parameters, are then used to calculate the four electronic (T_{2e}) and two nuclear (T_{2n}) spin-relaxation times, which constitute six duplicates of diagonal elements of the relaxation matrix in Liouville space for the four-level coupled electron-nuclear spin system, as outlined by Lee *et al.* [J. Chem. Phys. **98**, 3665-3689 (1993); hereafter LPF]. The four electronic- and two nuclear-spin relaxation times, are then found to be functions of τ_c, the correlation time, and a fluctuation-limiting factor, h, which, in turn, are estimated from the two experimentally known average values of the electronic and nuclear spin-relaxation times, $(T_{2e})_{\mathrm{exp}}$ and $(T_{2n})_{\mathrm{exp}}$, respectively, determined from the spin-echo correlation spectroscopy (SECSY) and echo-ELDOR signals data [LPF]. A rather narrow region of such τ_c and h values is found, giving a theoretical estimate to the values at its center: $\tau_c = 8.9 \times 10^{-8}$ s and $h = 0.11$, which are then used to calculate the time-dependent echo-ELDOR signal by exploiting the relevant Liouville-von Neumann equation, whose Fourier transform is found to be in very good agreement with that obtained by the experiment.

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Keywords: pulsed EPR, relaxation, thermal vibrations, two-dimensional echo-ELDOR, Liouville-von Neumann equation

1. Introduction

Pulsed electron paramagnetic resonance (EPR) can be used to characterize the dynamics of spin probes embedded in diamagnetic systems, using suitable theoretical tools for interpreting the effects of the molecular motions on the spectroscopic observables. In particular, one can exploit echo-ELDOR (electron-electron double resonance) signal, which is sensitive to the details of the relaxation of a spin system.

A general theoretical approach is employed in this paper to exploit the Liouville-von Neumann (LVN) equation, which describes the evolution of the density matrix, both in the presence and absence of a pulse, to calculate the effect of the relaxation caused by fluctuations of the spin-

Hamiltonian parameters (SHP), i.e. those of the elements of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices and their combinations, due to thermal motion of the molecule. In order to take into account relaxation rigorously, LVN equation is exploited, being an exact quantum-mechanical equation of motion for the density matrix.

In a previous study by Lee, Patyal and Freed [1] (hereafter LPF) on a γ-irradiated single crystal of malonic acid consisting of an electron-nuclear spin coupled system (electron spin $S = 1/2$; nuclear spin $I = 1/2$), the original theory of two-dimensional (2D)-EPR with nuclear modulation introduced by Gamliel and Freed [2] was extended to treat the problem in Liouville space. The combined effect of nuclear modulation and spin relaxation was there taken into account to calculate SECSY (Spin Echo Correlation Spectroscopy) and echo-ELDOR signals. However, the elements of the relaxation matrix used in LPF were defined in a phenomenological manner, using the relative intensities of the experimental peaks.

Information on correlation time, τ_{c}, of a given system is important to calculate time averages of physical quantities. The memory of a system to retain a certain property is dependent on the value of its correlation time, e.g. the magnetization due to a microwave pulse, as produced in a pulsed EPR experiment, such as SECSY, echo-ELDOR. The longer is the correlation time the longer is the physical property retained by the system.

The theory of coupled electron-nuclear system of a malonic-acid single crystal treated in LPF was improved recently by including the static spin Hamiltonian during the pulses [3] and extending the single-crystal calculations to the polycrystalline case [4]. It is the purpose of this paper to advance the theory further to treat relaxation due to molecular fluctuation as caused by thermal motion more rigorously for the coupled electron-nuclear system, with electron spin $S = 1/2$ and nuclear spin $I = 1/2$, using the first-order correction to the eigenvalues of the the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices due to the rather very small fluctuations of the spin-Hamiltonian parameters, proposed by Frezzato et al. [5]. The δ(SHP)), which are the time-dependent variation from the average values of the SHP, are here related to the fluctuation of the local director of the malonic-acid molecule, about the average orientation of the director, which is assumed to be along the molecular axis. These δ(SHP) are then used to calculate six elements of the relaxation matrix which are four electronic ($T_{2\mathrm{e}}$) and two nuclear ($T_{2\mathrm{n}}$) spin-relaxation times. Accordingly, the elements of the relaxation-matrix, used in Refs. [3, 4] for a coupled electron-nuclear system are here replaced by those calculated taking into account the fluctuation of SHP to treat the effect of relaxation on a pulsed-EPR signal. Knowing the average experimental values of ($T_{2\mathrm{e}}$) and ($T_{2\mathrm{n}}$) for the electron- and nuclear-spin transitions, respectively, one can estimate the values of the motional correlation time, τ_{c}, as well as an fluctuation-limiting factor, h.

Although the relaxation matrix can be calculated in a general form using the available open-source packages in Matlab e.g. Spinach [6], the algorithm for calculating the relaxation matrix introduced in this paper has the advantage that it deals with the fluctuation-relaxation problem in a more quantitative manner, since here the stochastic fluctuating parts of the spin Hamiltonian are defined explicitly in terms of the δ(SHP).

The organization of this paper is as follows. Section 2 describes the model of cylindrical fluctuation of the molecule, taking into account the relevant static and time-dependent fluctuating Hamiltonian. The auto-correlation function needed to calculate the relaxation matrix is discussed in Sec. 3. The six elements of the relaxation matrix, specifically four $T_{2\mathrm{e}}$ and two $T_{2\mathrm{n}}$ are calculated in Sec. 4. Estimation of the correlation time (τ_{c}) and a fluctuation-limiting factor, h, is carried out in Sec. 5. The concluding remarks and future perspectives are included in Sec. 6. The fluctuation spin Hamiltonian, as defined in terms of spherical tensors, is described in Appendix A. The procedure to exploit the LVN equation to calculate the echo-ELDOR signal is briefly outlined in Appendix B. The static Hamiltonian and the eigenvalue basis used to calculate the relaxation matrix are given in Appendix C.

2. Variation of SHP due to fluctuation of the molecule about the symmetry axis in the first order of perturbation

The static Hamiltonian $\hat{H}_0$ of an electron-nuclear spin-coupled system (electron spin $S = 1/2$; nuclear spin $I = 1/2$), neglecting non-secular terms in the high fields limit, is expressed as [1]

$$\hat{H}_0 = CS_z - \omega_\mathrm{n} I_z + AS_zI_z + \frac{1}{2}BS_zI_+ + \frac{1}{2}B^*S_zI_-, \tag{1}$$

where the coefficients C, A, B, B^* are defined in Eq. (C.2) of Appendix B in terms of the elements of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices and the Euler angles $\Omega(\alpha,\beta,\gamma)$, which relates the orientation of the principal axes of the $\tilde{\mathbf{g}}$-matrix, assumed to be coincident with those of the hyperfine ($\tilde{\mathbf{A}}$) matrix, to the Labratory frame with the Z-axis along the static magnetic field.

The matrix elements of the time-dependent fluctuating Hamiltonian, $\hat{H}_{1\alpha\beta}$ with $\alpha, \beta = a, b, c, d$ denoting the four energy-levels of the $S = 1/2; I = 1/2$ spin-coupled system, causing relaxation, can be written in general form as follows [1]:

$$\hat{H}_{1\alpha\beta} = \sum_{p=1}^{10} F^p(t)A^p_{\alpha\beta}; \quad \alpha,\beta = a,b,c,d, \tag{2}$$

where A^p are the spin operators in the laboratory frame that appear in the spin Hamiltonian, and $F^p(t)$ are the time-dependent fluctuating parts of the spin-Hamiltonian $\hat{H}_{1\alpha\beta}$, which depend on $\delta(\mathrm{SHP})[\delta g, \delta a, \delta F, \delta D, \delta F^{(2)}, \delta D^{(2)}]$ with $g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$, $a = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$, $F = \frac{2}{3}[g_{zz} - \frac{1}{2}(g_{xx} + g_{yy})]$, $D = \frac{2}{3}[A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})]$, $F^{(2)} = \frac{1}{2}(g_{xx} - g_{yy})$, $D^{(2)} = \frac{1}{2}(A_{xx} - A_{yy})$ (more details are given in Appendix B). The various $F^p(t)$ and $A^p_{\alpha\beta}$ in (2) are listed in Appendix A below [1].

2.1. Fluctuations of SHP due to thermal motion

For the electron-nuclear spin-coupled system of malonic acid crystals, it is assumed that phonon modulation of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices leads to spin relaxation that can be described by the Redfield equation applicable for motional narrowing. Then Eq. (1) for $\hat{H}_0$ is the thermal average of these fluctuations, and the relaxation matrix, $R_{\alpha\alpha',\beta\beta'}$, appearing in Redfield spin-relaxation equation [7]:

$$\frac{d\chi_{\alpha\alpha'}}{dt} = -i\omega_{\alpha\alpha'}\chi_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha',\beta\beta'}\chi_{\beta\beta'} \tag{3}$$

is composed of the small thermal fluctuations in these terms, defined explicitly in terms of the time-dependent interaction parameters, $\delta(\mathrm{SHP})$, appearing in Eqs. (A.1)-(A.10) of Appendix A below. The procedure to solve the LVN equation (3) is outlined in Appendix B. In order to calculate the effect of thermal vibrations in an irradiated malonic-acid crystal, the crystal can be treated in a statistical manner as an ensemble of a large number of malonic-acid molecules. Of these, consider a molecule representing the average of all the molecules in the ensemble undergoing the low-amplitude orientational motion about its equilibrium position due to thermal fluctuations. The resulting changes in SHP due to the fluctuations, $\delta(\mathrm{SHP})$, caused by thermal motion, will be considered here to cause the relaxation. These are taken into account as follows.

The average director frame ADF $= (x, y, z)$, of a malonic-acid molecule, is shown in Fig. 1, with the x axis being chosen along the average orientation of the director. The unit vector along the instantaneous orientation of the director will be denoted by the unit vector n, with the property that the averages of fluctuation of the director in the transverse, y and z directions, is zero: $\overline{n_\perp} = 0$. Now, the normalized $\mathbf{n}$ can be expressed as [5] (see Fig. 1)

$$\mathbf{n} = \sqrt{1 - 2\overline{n_\perp^2}}\,\mathbf{i} + n_\perp \mathbf{j} + n_\perp \mathbf{k}, \tag{4}$$

where $n_\perp$ is extremely small ($n_\perp \ll 1$), being the time-dependent fluctuating components of the director in the y and z directions and $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the unit vectors along the x, y, z axes, respectively. Choosing the ADF, with the y axis being coincident with the Y axis of the laboratory frame (LF), as shown in Fig. 2, the transformation from the LF frame to the ADF frame can be specified by the Euler angles $\Omega(\alpha\beta\gamma) = (0, -\theta, 0)$ in agreement with the echo-ELDOR experiment in LPF, where θ is the angle between the static magnetic field B_0 (assumed to be along the Z axis of the LF and the z-axis of ADF; the average director axis, $\overline{\mathbf{n}}$ is assumed to be along the x-axis of ADF, coincident with the principal-axes of $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices. At time scales longer than the correlation time, the spin Hamiltonian, averaged over the molecular orientations, can be used in the relevant LVN equation. Such an average spin Hamiltonian is constructed by inserting the fluctuating $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices which can be expressed in ADF, in general form, ($\boldsymbol{\sigma} = \tilde{\mathbf{g}}$ or $\tilde{\mathbf{A}}$) as

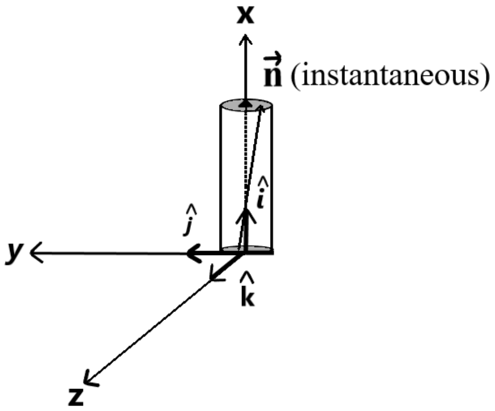


Figure 1. Fluctuations of the director of the molecule, represented by $\mathbf{n}(\mathbf{r})$. It fluctuates in such a way that the end points remain on the upper and bottom circular faces of the cylinder. The vector along the x-axis represents the average director orientation, which is along the symmetry axis (x) of the malonic-acid molecule.

$$\boldsymbol{\sigma} = \sigma_\perp \mathbb{1} + (\sigma_{||} - \sigma_\perp + \Delta\sigma_\perp \boldsymbol{\mathcal{E}})\mathbf{n}' \otimes \mathbf{n}' + \Delta\sigma_\perp \boldsymbol{\mathcal{E}}, \tag{5}$$

where, $\sigma_{||} = \sigma_{xx}$ and $\sigma_\perp = 1/2(\sigma_{yy} + \sigma_{zz})$, denoting the partially averaged fluctuating components parallel and perpendicular of those matrices, respectively, to the local director (x-axis); $\Delta\sigma_\perp$ is the rhombic parameter defined as $\Delta\sigma_\perp = 1/2(\sigma_{yy} - \sigma_{zz})$, $\otimes$ stands for the outer product, $\mathbb{1}$ is the diagonal 3×3 unit matrix, and $\boldsymbol{\mathcal{E}}$ is the matrix that defines the anisotropy in the xy-plane, as defined below

$$\boldsymbol{\mathcal{E}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{6}$$

In Eq. (5),

$$\mathbf{m} = \sqrt{1 - 2m_\perp^2}\,\mathbf{i} + m_\perp \mathbf{j} + m_\perp \mathbf{k}, \tag{7}$$

where $m_\perp = f n_\perp$, translates the spatial fluctuation into the fluctuation of $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices, assuming the same proportionality factor, f, for both.

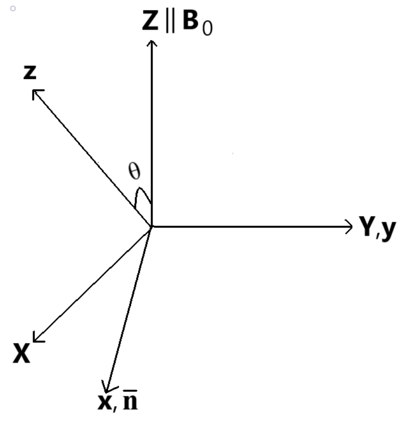


Figure 2. Relative orientations of, the laboratory frame (X, Y, Z) and the average director frame (x, y, z). The Euler angles $(0, \theta, 0)$ relate the two frames, so that $(\alpha, \beta = -\theta, \gamma) = (0°, -30°, 0°)$ for the echo-ELDOR signal simulated and plotted in Fig. 4. Here B_0 denotes the external magnetic field and $\overline{\mathbf{n}}$ denotes the average orientation of the director axis.

In writing Eq. (5), it is assumed that the fluctuations in the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices are due to their anisotropy [8, 9]. In accordance with the experimental values [10], $g_{yy} \approx g_{zz}$, so $\Delta g_\perp$ becomes negligible, so that Eq. (5), with axial $\tilde{g}$-matrix, is expressed as

$$\tilde{g} = \begin{pmatrix} g_\perp + (g_\parallel - g_\perp)(1 - 2m_\perp^2) & (g_\parallel - g_\perp)m_\perp\sqrt{1 - 2m_\perp^2} & (g_\parallel - g_\perp)m_\perp\sqrt{1 - 2m_\perp^2} \\ (g_\parallel - g_\perp)m_\perp\sqrt{1 - 2m_\perp^2} & g_\perp + (g_\parallel - g_\perp)m_\perp^2 & (g_\parallel - g_\perp)m_\perp^2 \\ ((g_\parallel - g_\perp)m_\perp\sqrt{1 - 2m_\perp^2} & (g_\parallel - g_\perp)m_\perp^2 & g_\perp + (g_\parallel - g_\perp)m_\perp^2 \end{pmatrix}. \tag{8}$$

As for the $\tilde{A}$-matrix without axial symmetry [10], one has

$$\tilde{A} = \begin{pmatrix} A_{xx} - 2m_\perp^2 & A' m_\perp\sqrt{1 - 2m_\perp^2} & A' m_\perp\sqrt{1 - 2m_\perp^2} \\ A' m_\perp\sqrt{1 - 2m_\perp^2} & A_{yy} + (A_{xx} - A_{yy})m_\perp^2 & A' m_\perp^2 \\ A' m_\perp\sqrt{1 - 2m_\perp^2} & A' m_\perp^2 & A_{zz} + (A_{xx} - A_{zz})m_\perp^2 \end{pmatrix}, \tag{9}$$

where $A' = A_{xx} - 1/2(A_{yy} - A_{zz})$ defined in Sec. 2. Note that, in the absence of any fluctuation, $m_\perp$ is equal to zero and Eqs. (8) and (9) become diagonal, $\tilde{g}$- and $\tilde{A}$- matrices. Since the amplitude of the fluctuation, is considered to be small, one can now invoke the first-order perturbation theory to calculate the effect of the fluctuations of the director on the eigenvalues of Eqs. (8) and (9), which are the corrections to the diagonal elements due to fluctuation, and ignore the off-diagonal terms. Accordingly, the fluctuation-perturbation corrections due to thermal motion to the diagonal elements of the $\tilde{g}$ and $\tilde{A}$ matrices are:

$$\begin{aligned}
\delta g_{xx} &= -2m_{\perp}^{2}(g_{\|} - g_{\perp});\\
\delta g_{yy} &= m_{\perp}^{2}(g_{\|} - g_{\perp});\\
\delta g_{zz} &= \delta g_{yy};\\
\delta A_{xx} &= -2m_{\perp}^{2}A';\\
\delta A_{yy} &= m_{\perp}^{2}(A_{xx} - A_{yy});\\
\delta A_{zz} &= m_{\perp}^{2}(A_{xx} - A_{zz}).
\end{aligned} \tag{10}$$

$\delta(SHP)$ are then calculated to be, in terms of fluctuating diagonal elements of $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices, expressed above in Eq. (10)

$$\begin{aligned}
\delta g &= \frac{1}{3}(\delta g_{xx} + \delta g_{yy} + \delta g_{zz});\\
\delta a &= \frac{1}{3}(\delta A_{xx} + \delta A_{yy} + \delta A_{zz});\\
\delta F &= \frac{2}{3}\Big(\delta g_{zz} - \frac{1}{2}(\delta g_{xx} + \delta g_{yy})\Big);\\
\delta D &= \frac{2}{3}\Big(\delta A_{zz} - \frac{1}{2}(\delta A_{xx} + \delta A_{yy})\Big);\\
\delta F^{(2)} &= \frac{1}{2}(\delta g_{xx} - \delta g_{yy});\\
\delta D^{(2)} &= \frac{1}{2}(\delta A_{xx} - \delta A_{yy}).
\end{aligned} \tag{11}$$

Using the fluctuation amplitudes given by Eqs. (10) and (11), and substituting them in Eqs. (A.1)-(A.10) of Sec. 2, one can calculate the fluctuation Hamiltoian in Sec. 2 in terms of the fluctuating parts of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices, which, in turn, depend on the transverse fluctuating component of the director orientation $m_{\perp}^{2}$.

3. Auto-correlation function, Spectral Density Function and Relaxation Matrix

3.1. Auto-correlation Function

The auto-correlation function, which relates the values separated by the time interval, is expressed as

$$P_{\alpha\beta\alpha'\beta'}(\tau) = \langle H_{1\alpha\beta}(t)H^{*}_{1\alpha'\beta'}(t-\tau)\rangle, \tag{12}$$

where $\langle \ldots \rangle$ denotes the time average over the ensemble. $P(\tau) = P(-\tau)$ and $P(\infty) = 0$ (Redfield [10], and the correlation time τ_{c} is governed by the condition that $P(\tau) \ll P(0)$ if $\tau \gg \tau_{\mathrm{c}}$.

Substituting Eq. (1) into Eq. (12), one obtains

$$P_{\alpha\beta\alpha'\beta'}(\tau) = \sum_{p,q}\langle A^{p}_{\alpha\beta}F^{p}(t)\Big(A^{q}_{\alpha'\beta'}F^{q}(t-\tau)\Big)^{*}\rangle = \sum_{p,q} A^{p}_{\alpha\beta}A^{q}_{\alpha'\beta'}\langle F^{p}(t)F^{q}(t-\tau)^{*}\rangle. \tag{13}$$

For the present calculation involving a malonic-acid crystal, it is considered that the phonon modulation of the $\tilde{A}$- and $\tilde{g}$-matrix elements leads to spin relaxation that can be described by the Redfield equation applicable to motional narrowing. The effect of the relaxation due to the time-dependent fluctuating part of the spin Hamiltonian is here taken into account quantitatively by using the values of δ(SHP) as outlined above in Sec. 2. It is noted that not only are the spin operators F^p orientation dependent, but their coefficients $A^p_{\alpha\beta}$ can also have substantial orientation dependence. The present calculations are made for a single crystal with well-defined orientations of the principal-axes of the $\tilde{\mathbf{g}}$- and hyperfine matrices. The various δ(SHP) are calculated using the model of Frezzato et al. [5], wherein one considers small thermal fluctuations of the director of the malonic-acid molecule in the plane transverse to the average director axis as shown in Fig. 1.

3.2. Spectral Density function

In order to calculate the elements of the relaxation matrix, one needs first to calculate the spectral density functions $J_{\alpha\beta\alpha'\beta'}(\omega)$ in frequency domain, related to the autocorrelation function through the Fourier transformation:

$$J_{\alpha\beta\alpha'\beta'}(\omega) = \frac{1}{2}\int\limits_{-\infty}^{\infty} e^{i\omega\tau} P_{\alpha\beta\alpha'\beta'}(\tau)d\tau. \tag{14}$$

Calculation of the ensemble average of the elements of the autocorrelation matrix, $P_{\alpha\beta\alpha'\beta'}$, and its spectral density function, $J_{\alpha\beta\alpha'\beta'}$, due to the fluctuating perturbation can be made by considering the correlation function between the fluctuating part of the spin Hamiltonian at times $t = 0$ and $t = \tau$: $\langle F^p(0)\big(F^q(\tau)\big)^*\rangle$. According to Eqs. (A.1)-(A.10) and (10)-(13), all of the autocorrelation functions $P_{\alpha\beta\alpha'\beta'}$ can be expressed in terms of the transverse components of the director i.e. $m_\perp^2$. The correlation functions between these components can be expressed as [5, 7]:

$$\langle m_\perp^2(\tau)m_\perp^2(0)\rangle = h^2 e^{-|\tau|/\tau_\mathrm{c}}. \tag{15}$$

Here, h represents the limiting factor for fluctuations in the transverse plane. Using now Eqs. (10)-(15), one obtains

$$J_{\alpha\beta\alpha'\beta'}(\omega) = \frac{1}{2}\sum_{p,q} A^p_{\alpha\beta}(A^q_{\alpha'\beta'})^* \int_{-\infty}^{\infty} h^2 e^{i\omega\tau-|\tau|/\tau_\mathrm{c}}d\tau. \tag{16}$$

The non-zero elements of the spectral density function are then calculated to be:

$$\begin{aligned} J_{\alpha\beta\alpha\beta}(\omega_{\alpha\beta}) &= \frac{\tau_\mathrm{c}}{1+(\omega_{\alpha\beta}\tau_\mathrm{c})^2}\sum_{p,q} A^p_{\alpha\beta}(A^q_{\alpha'\beta'})^* h^2; \\ J_{\alpha\alpha\beta\beta}(0) &= \tau_\mathrm{c}\sum_{p,q} A^p_{\alpha\alpha}(A^q_{\beta\beta})^* h^2; \\ J_{\alpha\alpha\alpha\alpha}(0) &= \tau_\mathrm{c}\sum_{p,q} A^p_{\alpha\alpha}(A^q_{\alpha\alpha})^* h^2. \end{aligned} \tag{17}$$

In Eq. (17) each α, β can be a, b, c, or d corresponding to the eigenvalues of $\hat{H}_0$ as described in Appendix A.

In order to calculate the relaxation matrix elements, the following properties of [7] are found useful:

$$J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha\beta}) = J_{\alpha\beta\alpha'\beta'}(-\omega_{\alpha\beta}) = J_{\beta'\alpha'\beta\alpha}(\omega_{\alpha\beta}) = J^*_{\beta\alpha\beta'\alpha'}(\omega_{\alpha\beta}). \tag{18}$$

4. Relaxation Matrix Elements

The relaxation matrix elements can be expressed in terms of $J_{\alpha\beta\alpha'\beta'}(\omega)$ as [7, 10]

$$\hat{\hat{R}}_{\alpha\alpha'\beta\beta'} = 2J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha'\beta'}) - \delta_{\alpha'\beta'}\sum_{\gamma} J_{\gamma\beta\gamma\beta}(\omega_{\gamma\beta}) - \delta_{\alpha\beta}\sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\omega_{\gamma\beta'}). \tag{19}$$

The matrix elements of T_1-type relaxation which contribute to T_2-type relaxation as well, in the eigenvalue-basis of the spin Hamiltonian of the spin-coupled system, $\hat{H}_0$ can be written as

$$\hat{\hat{R}}_{\alpha\alpha\beta\beta} = 2J_{\alpha\beta\alpha\beta}(\omega_{\alpha\beta}) - \delta_{\alpha\beta}\sum_{\gamma} J_{\gamma\beta\gamma\beta}(\omega_{\gamma\beta}) - \delta_{\alpha\beta}\sum_{\gamma} J_{\gamma\alpha\gamma\beta}(\omega_{\gamma\beta}). \tag{20}$$

It is seen from Eq. (20) that if $\alpha \neq \beta$,

$$\hat{\hat{R}}_{\alpha\alpha\beta\beta} = 2J_{\alpha\beta\alpha\beta}(\omega_{\alpha\beta}) \tag{21}$$

and from Eqs. (18) and (20), one obtains

$$\hat{\hat{R}}_{\alpha\alpha\beta\beta} = \hat{\hat{R}}_{\beta\beta\alpha\alpha}. \tag{22}$$

Equations (20)-(22) yield

$$\hat{\hat{R}}_{\alpha\alpha\alpha\alpha} = -\sum_{\beta(\neq\alpha)} \hat{\hat{R}}_{\alpha\alpha\beta\beta}. \tag{23}$$

From Eq. (19) by relabeling $\alpha'\beta\beta'$ as $\beta\beta\alpha$, respectively, one obtains the diagonal elements of the T_2-type relaxation as

$$\hat{\hat{R}}_{\alpha\beta\alpha\beta} = 2J_{\alpha\alpha\beta\eta}(0) - J_{\alpha\alpha\alpha\alpha}(0) - J_{\beta\beta\beta\beta}(0) + \frac{1}{2}\big(\hat{\hat{R}}_{\alpha\alpha\alpha\alpha} + \hat{\hat{R}}_{\beta\beta\beta\beta}\big). \tag{24}$$

Now using Eq. (18) after relabeling indices $\beta'\alpha'\beta$ as $\beta\beta\alpha$ respectively, one obtains

$$J_{\alpha\alpha\beta\beta}(0) = J_{\beta\beta\alpha\alpha}(0), \tag{25}$$

so that from Eqs. (24) and (25), it is seen that

$$\hat{\hat{R}}_{\alpha\beta\alpha\beta} = \hat{\hat{R}}_{\beta\alpha\beta\alpha}. \tag{26}$$

Finally, one obtains the non-zero elements of the relaxation matrix, $\hat{\hat{R}}_{\alpha\alpha'\beta\beta'}$, corresponding to the eigenstates $|a\rangle, |b\rangle, |c\rangle, |d\rangle$ of the static Hamiltonian, $\hat{H}_0$, for the $S = I = 1/2$ coupled system, using Eqs. (20)-(26) by making the correspondence of $\alpha\beta\alpha'\beta'$ to a, b, c, d, respectively, as follows:

$$\hat{\hat{R}}_{aabb} = 2J_{abab}(\omega_{ab}); \hat{\hat{R}}_{aacc} = 2J_{acac}(\omega_{ac}); \hat{\hat{R}}_{aadd} = 2J_{adad}(\omega_{ad}); \tag{27}$$

$$\hat{\hat{R}}_{bbaa} = \hat{\hat{R}}_{aabb}; \hat{\hat{R}}_{bbcc} = 2J_{bcbc}(\omega_{bc}); \hat{\hat{R}}_{bbdd} = 2J_{bdbd}(\omega_{bd}); \tag{28}$$

$$\hat{\hat{R}}_{ccaa} = \hat{\hat{R}}_{aacc}; \hat{\hat{R}}_{ccbb} = \hat{\hat{R}}_{bbcc}; \hat{\hat{R}}_{bbdd} = 2J_{cdcd}(\omega_{cd}); \tag{29}$$

$$\hat{\hat{R}}_{ddaa} = \hat{\hat{R}}_{aadd}; \hat{\hat{R}}_{ddbb} = \hat{\hat{R}}_{bbdd}; \hat{\hat{R}}_{ddcc} = \hat{\hat{R}}_{ccdd}; \tag{30}$$

$$\begin{gathered}
\hat{\hat{R}}_{aaaa} = -\Big(\hat{\hat{R}}_{aabb} + \hat{\hat{R}}_{aacc} + \hat{\hat{R}}_{aadd}\Big);\ \hat{\hat{R}}_{bbbb} = -\Big(\hat{\hat{R}}_{bbaa} + \hat{\hat{R}}_{bbcc} + \hat{\hat{R}}_{bbdd}\Big);\\
\hat{\hat{R}}_{cccc} = -\Big(\hat{\hat{R}}_{ccaa} + \hat{\hat{R}}_{ccbb} + \hat{\hat{R}}_{ccdd}\Big);\ \hat{\hat{R}}_{dddd} = -\Big(\hat{\hat{R}}_{ddaa} + \hat{\hat{R}}_{ddbb} + \hat{\hat{R}}_{ddcc}\Big);
\end{gathered} \tag{31}$$

$$\begin{gathered}
\hat{\hat{R}}_{abab} = 2J_{aabb}(0) - J_{aaaa}(0) - J_{bbbb}(0) + \Big(\hat{\hat{R}}_{aaaa} + \hat{\hat{R}}_{bbbb}\Big)/2;\\
\hat{\hat{R}}_{acac} = 2J_{aacc}(0) - J_{aaaa}(0) - J_{cccc}(0) + \Big(\hat{\hat{R}}_{aaaa} + \hat{\hat{R}}_{cccc}\Big)/2;\\
\hat{\hat{R}}_{adad} = 2J_{aadd}(0) - J_{aaaa}(0) - J_{dddd}(0) + \Big(\hat{\hat{R}}_{aaaa} + \hat{\hat{R}}_{dddd}\Big)/2;
\end{gathered} \tag{32}$$

$$\begin{aligned}\hat{\hat{R}}_{baba} &= \hat{\hat{R}}_{abab};\\ \hat{\hat{R}}_{bcbc} &= 2J_{bbcc}(0) - J_{bbbb}(0) - J_{cccc}(0) + \left(\hat{\hat{R}}_{bbbb} + \hat{\hat{R}}_{cccc}\right)/2;\\ \hat{\hat{R}}_{bdbd} &= 2J_{bbdd}(0) - J_{bbbb}(0) - J_{dddd}(0) + \left(\hat{\hat{R}}_{bbbb} + \hat{\hat{R}}_{dddd}\right)/2;\end{aligned} \tag{33}$$

$$\begin{aligned}\hat{\hat{R}}_{caca} &= \hat{\hat{R}}_{acac}; \hat{\hat{R}}_{cbcb} = \hat{\hat{R}}_{bcab};\\ \hat{\hat{R}}_{cdcd} &= 2J_{ccdd}(0) - J_{cccc}(0) - J_{dddd}(0) + \left(\hat{\hat{R}}_{cccc} + \hat{\hat{R}}_{dddd}\right)/2;\end{aligned} \tag{34}$$

$$\hat{\hat{R}}_{dada} = \hat{\hat{R}}_{adad}; \hat{\hat{R}}_{dbdb} = \hat{\hat{R}}_{bdad}; \hat{\hat{R}}_{dcdc} = \hat{\hat{R}}_{cdcd}. \tag{35}$$

Except for the above, all other elements

$$\hat{\hat{R}}_{\alpha\beta\alpha'\beta'}(\omega_{\eta\zeta}) = 0, \tag{36}$$

where each $\alpha, \beta, \alpha', \beta', \eta, \zeta$ can be a, b, c, or d.

5. Estimation of the correlation time (τ_c)

In order to estimate the amplitude of the fluctuation and the correlation time, one first needs to calculate the relaxation matrix elements as defined by Eq. (19). Following the procedure described in Sec. 2 and using Eqs. (27)-(35), the elements of the relaxation matrix can be calculated in the eigenvalue basis as functions of the correlation time, τ_c, and the amplitude of fluctuation (h^2). Then, the relaxation matrix elements can be expressed as functions of τ_c and h^2, i.e. $\hat{\hat{R}}_{\alpha\beta\alpha\beta} = \hat{\hat{R}}_{\alpha\beta\alpha\beta}(\tau_c, h^2)$. Since the six T_2 values for the various electron and nuclear spin transitions are related to the relaxation matrix elements, specifically

$$\begin{aligned}(T_2)_{ac} &= 1/\hat{\hat{R}}_{1313}; \quad (T_2)_{bd} = 1/\hat{\hat{R}}_{2424};\\ (T_2)_{ad} &= 1/\hat{\hat{R}}_{1414}; \quad (T_2)_{bc} = 1/\hat{\hat{R}}_{2323};\\ (T_2)_{ab} &= 1/\hat{\hat{R}}_{1212}; \quad (T_2)_{cd} = 1/\hat{\hat{R}}_{3434},\end{aligned} \tag{37}$$

where the energy levels a, b, c, d are defined in appendix A below, one can calculate $(T_{2e})_{\alpha\beta}(\tau_c, h^2) = (T_{2e})_{\text{exp}}$ and $(T_{2n})_{\alpha\beta}(\tau_c, h^2) = (T_{2n})_{\text{exp}}$; $\alpha, \beta = a, b, c, d$ from the calculated values of the elements of the relaxation matrix. Note that in [1], only two experimental values, $(T_{2e})_{\text{exp}}$ and $(T_{2n})_{\text{exp}}$, were estimated, so it is assumed here that $(T_2)_{ac} = (T_2)_{bd} = (T_2)_{ad} = (T_2)_{bc} = T_{2\text{e}}$ and $(T_2)_{cd} = (T_2)_{ab} = T_{2\text{n}}$.

In Fig. 3, all values of $(T_2)_{\alpha\beta}; \alpha \neq \beta$ corresponding to the four different electron spin transitions $\Big((T_2)_{ac}, (T_2)_{bd}, (T_2)_{ad}, (T_2)_{bc}\Big)$ and two different nuclear spin transitions $\Big((T_2)_{cd}, (T_2)_{ab}\Big)$ are plotted as functions of τ_c, h^2 , using the experimental values, reported in [1]: $T_{2\text{e}} = 900\,\text{ns}$ and $T_{2\text{n}} = 22\,\mu\text{s}$. One then obtains six lines as shown in Fig. 3 in the (τ_c, h^2) plane. The average values of ($\tau_c = 8.9 \times 10^{-8}$ s, $h^2 = 1.18 \times 10^{-2}$), i.e. those situated at the center of this area are now chosen to calculate the relaxation-matrix elements as defined in Eq. (19). This matrix is then used in the simulation of the time-domain echo-ELDOR signal and its Fourier transform (FT), as shown in Fig. 4a, together with the simulated FT using the phenomenological relaxation matrix Fig. 4b, the experimental FT as reported in [1] Fig. 4c and simulated FT in the absence of the relaxation matrix Fig. 4d. Comparing the FT of this signal with the experimental signal reported in [1], a very good agreement is found; as well, it is also in good agreement with that simulated phenomenologically. The simulation without relaxation (Fig. 4d) is distinctly different from that with relaxation (Fig. 4a), indicating that relaxation is an important effect to consider.

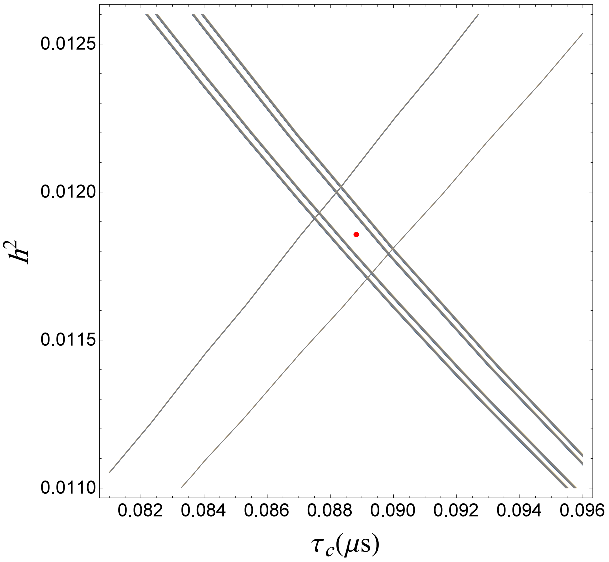


Figure 3. Contour plots of $(T_2)_{ac}, (T_2)_{bd}, (T_2)_{ad}, (T_2)_{bc}$ for the experimental value $(T_{2e})_{\exp} = 900\,\mathrm{ns}$ and those for $(T_2)_{ab}, (T_2)_{cd}$, for the experimental value $(T_{2n})_{\exp} = 22\,\mu\mathrm{s}$ as a function of the correlation time τ_c and h^2 .The red point inside the overlapping region represents the average values $\tau_c = 8.9 \times 10^{-8}$ s and $h^2 = 1.18 \times 10^{-2}$. They are used for simulation of the echo-ELDOR signal Shown in Fig. 3.

6. Conclusions and Future Perspectives

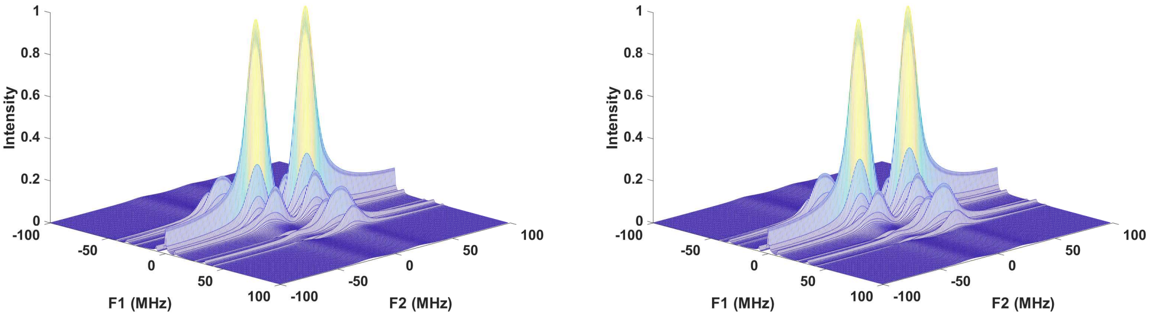
6.1. Conclusions

The salient features of the present work dealing with the calculation of echo-ELDOR pulse EPR signal, taking into account relaxation due to fluctuation of malonic acid molecules caused by thermal motion in a γ-irradiated malonic acid crystal of an electron-nuclear spin-coupled system $(S = 1/2; I = 1/2)$ are as follows.

(i) A model is presented of how to calculate the relaxation matrix due to changes in the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices characterizing an electron-nuclear spin coupled system of a molecule due to thermal motion causing small fluctuations of the molecule in the transverse plane to the symmetry axis.

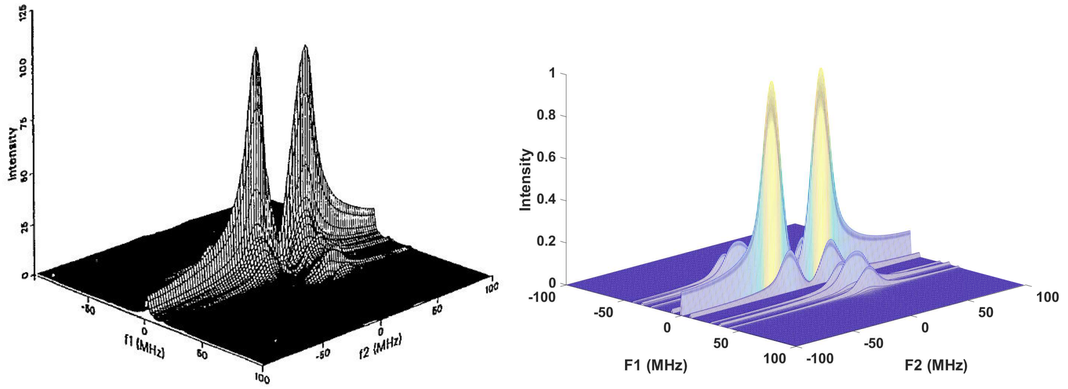
(ii) Using the experimental values of the electronic and nuclear spin relaxation times $(T_{2e})_{\exp}$ and $(T_{2n})_{\exp}$, respectively, the correlation time (τ_c) and the value of a fluctuation-limiting factor (h) have been estimated, assuming the director axis of the molecule to be fluctuating within a cylindrical volume of a rather small cross section about the symmetry axis of the molecule.

(iii) When the four calculated T_{2e} and the two calculated T_{2e} (Sec. 5) are plotted versus the correlation time (τ_c) and the effective fluctuation parameter (h^2), a rather narrow region is obtained in the (τ_c, h^2) plane (Fig. 3) that corresponds to the experimental values of $(T_{2e})_{\exp}$ and $(T_{2n})_{\exp}$. The average values of the correlation time (τ_c and h^2 at the center of this region $(\tau_c = 8.9 \times 10^{-8}$ s and $h^2 = 1.18 \times 10^{-2})$. When these values are used to simulate the echo-ELDOR signal, a very good agreement with the experimental echo-ELDOR signal is found.



(a) Relaxation matrix calculated in this work

(b) Phenomenological relaxation matrix introduced in LPF



(c) experimental

(d) Without relaxation

Figure 4. (a) Fourier transform of the simulated echo-ELDOR spectrum with the relaxation matrix calculated in this work (b) with phenomenological relaxation matrix introduced in LPF (c) experimental Fourier transforms of the echo-ELDOR signal (d) simulated without any relaxation at the orientations $(\alpha, \beta = -\theta, \gamma) = (0°, -30°, 0°)$, with the mixing times $T_{\mathrm{m}} = 40\,\mu$s. The correlation time $\tau_{\mathrm{c}} = 8.9 \times 10^{-8}$ s and $h^2 = 1.18 \times 10^{-2}$, as found here to be the best-fit values, are used in the simulation of (a). An inhomogeneous Gaussian broadening along the f_2 axis with the width $\Delta = 5$ MHz is used in the simulations. Figure (a), drawn using the best-fit values, shows a very good agreement with the experiment (Fig. (c)) and simulated spectrum with phenomenological relaxation matrix introduced in LPF. The experimental Figure (c) is reproduced with the permission of the authors of [1].

6.2. Future Perspectives

The simple treatment of fluctuation of the director in the transverse plane to the symmetry axis of malonic-acid molecule considered in this paper can be extended to treat more sophisticated models of fluctuation, e.g. that mentioned in Appendix B of Freed et al. [11], wherein one considers quantum mechanical equation of the spherical top in an axially symmetric restoring potential. Efforts are in progress to calculate the spin relaxation matrix due to thermal motion of malonic acid crystal using this model. Ultimately, more sophisticated models of treating relaxation due to thermal motion in pulsed EPR can be developed following our model.

Acknowledgments

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Appendices

A. The fluctuation spin Hamiltonian

The matrix elements of the time-dependent Hamiltonian, $\hat{H}_{1\alpha\beta}$, used in Eq. (2) of Sec. 2 are listed in this appendix for the various terms of the static Hamiltonian as denoted by p, as follows:
$p = 1$: Isotropic g factor (coefficient of S_z):

$$\begin{gathered} F^{(1)}(t) = \frac{\beta_e B_0}{\hbar}\delta g; \;\; A^{(1)}_{ac} = A^{(1)}_{bd} = A^{(1)}_{ad} = A^{(1)}_{bc} = A^{(1)}_{ab} = A^{(1)}_{cd} = 0; \\ A^{(1)}_{aa} = A^{(1)}_{bb} = A^{(1)}_{cc} = A^{(1)}_{dd} = 1/2; \end{gathered} \tag{A.1}$$

$p = 2$: Anisotropic g factor (coefficient of S_z):

$$\begin{gathered} F^{(2)}(t) = \delta F(3\cos^2\beta - 1)/2 + \delta F^{(2)}\sin^2\beta\cos(2\gamma) \\ A^{(2)}_{ac} = A^{(2)}_{bd} = A^{(2)}_{ad} = A^{(2)}_{bc} = A^{(2)}_{ab} = A^{(2)}_{cd} = 0; \\ A^{(2)}_{aa} = A^{(2)}_{bb} = A^{(2)}_{cc} = A^{(2)}_{dd} = 1/2; \end{gathered} \tag{A.2}$$

$p = 3$: Anisotropic g factor (coefficient of $S_+ + S_-$):

$$\begin{gathered} F^{(3)}(t) = \frac{3\,\delta F}{8}\sin(2\beta) - \frac{\delta F^{(2)}}{4}\sin(2\beta)\cos(2\gamma) \\ A^{(3)}_{ac} = A^{(3)}_{bd} = m_1^2; \;\; A^{(3)}_{ad} = A^{(3)}_{bc} = m_2^2; \\ A^{(3)}_{ab} = A^{(3)}_{cd} = A^{(3)}_{aa} = A^{(3)}_{bb} = A^{(3)}_{cc} = A^{(3)}_{dd} = 0; \end{gathered} \tag{A.3}$$

$p = 4$: Isotropic hyperfine factor (coefficient of $S_z I_z$):

$$\begin{gathered} F^{(4)}(t) = -2\pi\delta a; \;\; A^{(4)}_{ac} = A^{(4)}_{bd} = A^{(4)}_{ad} = A^{(4)}_{bc} = 0; \\ A^{(4)}_{ab} = \frac{1}{2}[\mathrm{Re}(c_1^* c_2)]; \;\; A^{(4)}_{cd} = \frac{1}{2}[\mathrm{Re}(c_3^* c_4)]; \\ A^{(4)}_{aa} = A^{(4)}_{bb} = \frac{1}{4}\sqrt{|c_1|^2 - |c_2|^2}; \;\; A^{(4)}_{cc} = A^{(4)}_{dd} = \frac{1}{4}\sqrt{|c_3|^2 - |c_4|^2}; \end{gathered} \tag{A.4}$$

$p = 5$: Isotropic hyperfine factor (coefficient of $\frac{1}{2}[S_+ I_- + S_- I_+]$):

$$\begin{gathered} F^{(5)}(t) = 0; \;\; A^{(5)}_{ac} = \frac{1}{2}|c_2^* c_3|; \;\; A^{(5)}_{bd} = \frac{1}{2}|c_1^* c_4|; \;\; A^{(5)}_{ad} = \frac{1}{2}|c_2^* c_4|; \\ A^{(5)}_{bc} = \frac{1}{2}|c_1^* c_3|; \;\; A^{(5)}_{ab} = A^{(5)}_{cd} = A^{(5)}_{aa} = A^{(5)}_{bb} = A^{(5)}_{cc} = A^{(5)}_{dd} = 0; \end{gathered} \tag{A.5}$$

$p = 6$: Anisotropic hyperfine factor (coefficient of $S_z I_z$)

$$\begin{gathered} F^{(6)}(t) = 2\pi\Big(\frac{\delta D}{2}(3\cos^2(\beta) - 1) + \delta D^{(2)}\sin^2(\beta)\cos(2\gamma)\Big); \\ A^{(6)}_{ac} = A^{(6)}_{bd} = A^{(6)}_{ad} = A^{(6)}_{bc} = 0; \;\; A^{(6)}_{ab} = \frac{1}{2}[\mathrm{Re}(c_1^* c_2)]; \;\; A^{(6)}_{cd} = \frac{1}{2}[\mathrm{Re}(c_3^* c_4)]; \\ A^{(6)}_{aa} = A^{(6)}_{bb} = \frac{1}{4}\sqrt{|c_1|^2 - |c_2|^2}; \;\; A^{(6)}_{cc} = A^{(6)}_{dd} = \frac{1}{4}\sqrt{|c_3|^2 - |c_4|^2}; \end{gathered} \tag{A.6}$$

$p = 7$: Anisotropic hyperfine factor (coefficient of $-\frac{1}{4}[S_+ I_- + S_- I_+]$):

$$\begin{gathered} F^{(7)}(t) = 0; \;\; A^{(7)}_{ac} = \frac{1}{2}|c_2^* c_3|; \;\; A^{(7)}_{bd} = \frac{1}{2}|c_1^* c_4|; \;\; A^{(7)}_{ad} = \frac{1}{2}|c_2^* c_4|; \\ A^{(7)}_{bc} = \frac{1}{2}|c_1^* c_3|; \;\; A^{(7)}_{ab} = A^{(7)}_{cd} = A^{(7)}_{aa} = A^{(7)}_{bb} = A^{(7)}_{cc} = A^{(7)}_{dd} = 0; \end{gathered} \tag{A.7}$$

$p = 8$: Anisotropic hyperfine factor (coefficient of $S_z I_- + S_z I_+$)

$$\begin{gathered} F^{(8)}(t) = 2\pi\Big(\frac{3\,\delta D}{8}\sin(2\beta) - \frac{\delta D^{(2)}}{4}\sin(2\beta)\cos(2\gamma)\Big); \\ A^{(8)}_{ac} = A^{(8)}_{bd} = A^{(8)}_{ad} = A^{(8)}_{bc} = 0;\;\; A^{(8)}_{ab} = \frac{1}{2}(|c_1|^2 - |c_2|^2); \\ A^{(8)}_{cd} = \frac{1}{2}(|c_3|^2 - |c_4|^2);\;\; A^{(8)}_{aa} = A^{(8)}_{bb} = \mathrm{Re}(c_1^* c_2);\;\; A^{(8)}_{cc} = A^{(8)}_{dd} = \mathrm{Re}(c_3^* c_4); \end{gathered} \tag{A.8}$$

$p = 9$: Anisotropic hyperfine factor (coefficient of $S_+ I_z + S_- I_z$):

$$\begin{gathered} F^{(9)}(t) = 0;\;\; A^{(9)}_{ac} = \frac{1}{2}|c_1^* c_3 - c_2^* c_4|;\;\; A^{(9)}_{bd} = \frac{1}{2}|c_1^* c_3 - c_2^* c_4|; \\ A^{(9)}_{ad} = \frac{1}{2}|c_1^* c_4 + c_2^* c_3|;\;\; A^{(9)}_{bc} = \frac{1}{2}|c_1^* c_4 + c_2^* c_3|; \\ A^{(9)}_{ab} = A^{(9)}_{cd} = A^{(9)}_{aa} = A^{(9)}_{bb} = A^{(9)}_{cc} = A^{(9)}_{dd} = 0; \end{gathered} \tag{A.9}$$

$p = 10$: Anisotropic hyperfine factor (coefficient of $S_- I_- + S_+ I_+$):

$$\begin{gathered} F^{(10)}(t) = 2\pi\Big(\frac{3\,\delta D}{8}\sin^2(\beta) - \frac{\delta D^{(2)}}{4}(1 + \cos^2(\beta)\cos(2\gamma)\Big); \\ A^{(10)}_{ac} = \frac{1}{4}|c_1^* c_4|;\;\; A^{(10)}_{bd} = \frac{1}{4}|c_2^* c_3|;\;\; A^{(10)}_{ad} = \frac{1}{4}|c_1^* c_3|; A^{(10)}_{bc} = \frac{1}{2}|c_2^* c_4|; \\ A^{(10)}_{ab} = A^{(10)}_{cd} = A^{(10)}_{aa} = A^{(10)}_{bb} = A^{(10)}_{cc} = A^{(10)}_{dd} = 0. \end{gathered} \tag{A.10}$$

Here, the quantities m_1, m_2, $c_i (i = 1, 2, 3, 4)$ appearing in Eqs. (A.3)-(A.10) are listed in Appendix C.

B. Solution of Liouville-von Neumann (LVN) equation

This appendix provides a brief outline of how to solve the LVN equation as applied to the present case. Full details of how to solve the LVN equation are described in Refs. [3,4].

The evolution of the reduced density matrix $\chi(t) = \rho(t) - \rho_{\mathrm{eq}}$, where ρ_{eq} is the equilibrium density matrix, proportional to S_z, taking into account the relaxation effects, is expressed in Liouville space, as follows [7,11–15]

$$\frac{d\hat{\hat{\chi}}}{dt} = -i\hat{\hat{L}}\hat{\hat{\chi}} - \hat{\hat{R}}\hat{\hat{\chi}}, \tag{B.1}$$

where, in a chosen basis, $\hat{\hat{R}}$ is the relaxation matrix and $\hat{\hat{L}}$ is the Liouvillian matrix. The solution of Eq. (B.1), after time t, can be expressed as

$$\hat{\hat{\chi}}(t) = e^{-(t-t_0)\hat{\hat{L}}'}\hat{\hat{\chi}}(t_0). \tag{B.2}$$

Under the free evolution, $\hat{\hat{L}}'$ in Eq. (B.2) is expressed in the direct-prodeuct electron-nuclear spin space as

$$\hat{\hat{L}}' \equiv i\hat{\hat{L}} + \hat{\hat{R}} = i\Big[I_n \otimes \hat{H}_0 - (\hat{H}_0)^{\mathrm{T}} \otimes I_{\mathrm{n}}\Big] + \hat{\hat{R}}. \tag{B.3}$$

In Eq. (B.3), $\hat{H}_0$ is the static Hamiltonian, described in Appendix C below, I_{n} is the unit matrix in the nuclear spin space, symbol T denotes the transpose operation and $\otimes$ refers to direct product.

On the other hand, in the presence of a pulse, $\hat{\epsilon}$, the Liouvillian is:

$$\hat{\hat{L}}' \equiv i\Big[I_{\mathrm{n}} \otimes (\hat{H}_0 + \hat{\epsilon}) - (\hat{H}_0 + \hat{\epsilon})^{\mathrm{T}} \otimes I_{\mathrm{n}}\Big]. \tag{B.4}$$

Here, the relaxation matrix during the pulses is not taken to account since it has negligible effect as shown in [3]. In Eq. (B.4), $\hat{\epsilon}$ is expressed, in the rotating frame, in which the calculations are being made, as

$$\epsilon(t) = B_1\gamma_\mathrm{e}(S_x\cos(\phi) + S_y\sin(\phi), \tag{B.5}$$

where ϕ and B_1 are the phase angle and the amplitude of the pulse magnetic field, respectively, and $\gamma_\mathrm{e}B_1t_p = \pi/2$ with t_p is the duration of the $\pi/2$ pulse. For the calculation of the final density matrix, ρ_f, for the echo-ELDOR signal, one uses Eq. (B.2) with $\hat{\hat{L}}'$ defined in Eqs. (B.3) and (B.4) for the evolution of the density matrix in the absence and presence of a pulse, respectively. In particular, in the present case, the calculations are made for the pulse sequences shown in Fig. 5 for the coherent pathway S_{C^-}. There are used two times, t_1 and t_2, which are stepped in the experiment (Fig. 5).

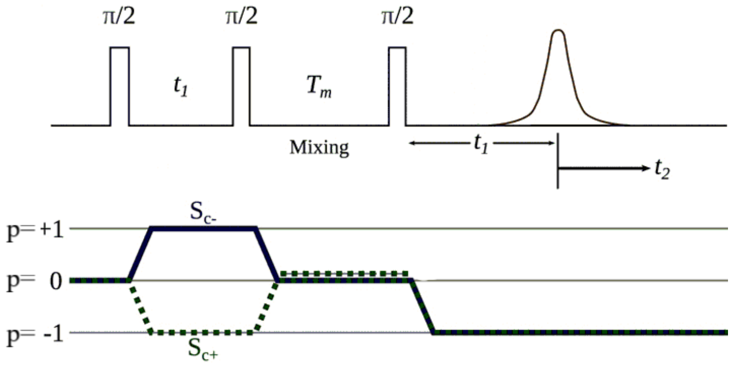

Figure 5. The pulse sequence for obtaining echo-ELDOR signal. The t_1 time between the first two pulses and the t_2 time from the echo are stepped in the experiment. Here T_m is the mixing time. (Bottom) The S_{C^-} and S_{C^+} coherence pathways, as shown by continuous and dotted lines, respectively, used for calculating the echo-ELDOR signal for an unpaired electron ($S = 1/2$) interacting with a single nucleus ($I = 1/2$). Here p is the coherence order, which represents transverse magnetization, corresponding to spins rotating in a plan perpendicular to the external field [16].

The 2D time-domain signal is calculated from ρ_f as follows:

$$S(t_1, t_2) = \mathrm{Tr}(S_+\rho_\mathrm{f}) = \mathrm{Tr}((S_x + iS_y)\rho_\mathrm{f}). \tag{B.6}$$

The Fourier transform (FT) of the two-dimensional (2D) time domain signal $S(t_1, t_2)$, is the corresponding 2D-FT signal, $S(\omega_1, \omega_2)$. In the real experiment in LPF [1], there is inhomogeneous broadening along the ω_2 axis, but the refocusing with respect to t_1, in the echo experiment cancels out the inhomogeneous broadening along the ω_1 axis. The Gaussian inhomogeneous broadening effect in the frequency-domain along $\omega_2(= 2\pi\nu)$, corresponding to the step time t_2, as depicted in Fig. 5, is taken into account by multiplying the time-domain signal with $e^{-2(\pi\Delta t_2)^2}$ with $\Delta = 5\,\mathrm{MHz}$ [1].

Rotating Frame. The calculations are carried in the rotating frame. Since the spin is in resonance, the effective magnetic field $B_\mathrm{eff} = B - \hbar\omega/g\mu_\mathrm{B}$ becomes zero. The coherence pathways S_{C^-} and S_{C^+} for obtaining echo-ELDOR signal, used commonly, are depicted in Fig. 5.

In the present paper, the echo-ELDOR signal is calculated over the coherent pathway S_{C^-} in accordance with that used by LPF for the experiment as depicted in Fig 4(d) for the orientation $(\alpha, \beta = -\theta\,\gamma) = (0°, -30°, 0°)$. The values of the Spin-Hamiltonian parameters and the external magnetic field (B_0) used are as follows [10]: the $\pi/2$ pulse is of duration

$\sim 5\,\text{ns}$ [1]; $\omega_\text{n} = 14.5\,\text{MHz}$; $\tilde{g} = (g_{xx}, g_{yy}, g_{zz}) = (2.0026, 2.0035, 2.0033)$; $\tilde{A} = (A_{xx}, A_{yy}, A_{zz}) = (-61.0\,\text{MHz}, -91.0\,\text{MHz}, -29.0\,\text{MHz})$. It is noted that within the experimental error of ± 0.0001, $g_{yy} \simeq g_{zz}$, justifying the use of the symmetry of fluctuation amplitudes in the directions transverse to the symmetry axis.

C. The static spin Hamiltonian

In this appendix the static spin Hamiltonian, eigenvalues and eigenvectors, and combinations of $\tilde{\mathbf{g}}$, $\tilde{\mathbf{A}}$ matrix elements appearing in the eigenvalues as used in Sec. 2 are considered.

For the specific case of a single nucleus ($I = 1/2$) interacting with an unpaired electron ($S = 1/2$) by the hyperfine interaction in the presence of an external magnetic field, where the $\tilde{\mathbf{A}}$-matrix has coincident principal axes to that of the $\tilde{\mathbf{g}}$-matrix, the static Hamiltonian can be expressed as [1]

$$\hat{H}_0 = CS_z - \omega_\text{n} I_z + AS_z I_z + \frac{1}{2} B S_z I_+ + \frac{1}{2} B^* S_z I_-. \tag{C.1}$$

The coefficients in Eq. (C.1) are expressed as follows:

$$\begin{aligned} C &= \frac{\beta_\text{e} B_0}{\hbar}\Big[\overline{g} + \frac{f}{2}(3\cos^2(\beta) - 1) + F^{(2)}\sin^2(\beta)\cos(2\gamma)\Big]; \\ A &= -2\pi\Big[\overline{a} + \frac{D}{2}(3\cos^2(\beta) - 1) + D^{(2)}\sin^2(\beta)\cos(2\gamma)\Big]; \\ B &= -4\pi\Big[\frac{3D}{4}\sin(\beta)\cos(\beta) - \frac{D^{(2)}}{2}\sin(\beta)[\cos(\beta)\cos(2\gamma) - i\sin(2\gamma)]\Big]. \end{aligned} \tag{C.2}$$

Here $\overline{g}(\overline{a})$, is the isotropic part and $D(F)$, $D^{(2)}(F^{(2)})$ are the axiality and rhombicity parameters of the $\tilde{\mathbf{g}}$- and $\tilde{\mathbf{A}}$-matrices, respectively, as defined is Sec. 2.

The eigenvalues of the Hamiltonian, $\hat{H}_0$, as given by Eq. (C.1) are [1]

$$E_a = C/2 + 1/2\omega_\alpha; E_b = C/2 - 1/2\omega_\alpha; E_c = -C/2 - 1/2\omega_\beta; E_d = C/2 + 1/2\omega_\beta, \tag{C.3}$$

where $\omega_\alpha, \omega_\beta$ are

$$\omega_\alpha = \left[\left(\frac{A}{2} - \omega_\text{n}\right)^2 + \left|\frac{B}{2}\right|^2\right]^{1/2}, \quad \omega_\beta = \left[\left(\frac{A}{2} + \omega_\text{n}\right)^2 + \left|\frac{B}{2}\right|^2\right]^{1/2}, \tag{C.4}$$

and the eigenvectors denoted by the indices a, b, c, d are defined as follows:

$$|a\rangle = \begin{pmatrix} c_1 \\ -c_2 \\ 0 \\ 0 \end{pmatrix}; \quad |b\rangle = \begin{pmatrix} c_2 \\ c_1 \\ 0 \\ 0 \end{pmatrix}; \quad |c\rangle = \begin{pmatrix} 0 \\ 0 \\ c_3 \\ -c_4 \end{pmatrix}; \quad |d\rangle = \begin{pmatrix} 0 \\ 0 \\ c_4 \\ c_3 \end{pmatrix}. \tag{C.5}$$

In Eq.(C.5) the coefficients c_i $(i = 1, 2, 3, 4)$ are:

$$\begin{aligned} c_1 &= \frac{1}{\sqrt{2}}\left[1 \pm \frac{(A/2) - \omega_\text{n}}{\omega_\alpha}\right]^{1/2}; \quad c_2 = -\frac{1}{\sqrt{2}}\left[1 \mp \frac{(A/2) - \omega_\text{n}}{\omega_\alpha}\right]^{1/2}; \\ c_3 &= \frac{1}{\sqrt{2}}\left[1 + \frac{(A/2) + \omega_\text{n}}{\omega_\beta}\right]^{1/2}; \quad c_4 = -\frac{1}{\sqrt{2}}\left[1 - \frac{(A/2) - \omega_\text{n}}{\omega_\beta}\right]^{1/2}. \end{aligned} \tag{C.6}$$

Here ω_n is the nuclear Larmor frequency. It is noted that $\omega_\alpha, \omega_\beta$ and c_i depend on the molecular orientation, because of the dependence of A and B on the Euler angles. In Eqs. (C.6), in the coefficients c_1 and c_2, the upper signs must be used when $A/2 > \omega_\text{n}$,whereas the lower signs must be used when $A/2 < \omega_\text{n}$. The value of A depends on the orientation. For the particular orientation considered here, $A/2 > \omega_\text{n}$ therefore, only the upper signs are applicable.

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