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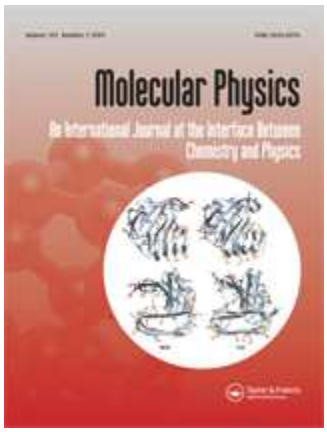

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Journal:	*Molecular Physics*
Manuscript ID:	TMPH-2007-0111.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	11-Jul-2007
Complete List of Authors:	DELIGIANNAKIS, YIANNIS; University of Ioannina, Environmental & Natural Resources Management
Keywords:	EPR, dipolar interaction, relaxation enhancement, g-anisotropy, Distance

Enhancement of Electron Spin Relaxation (T_1) in Rigid Systems by Rapidly Relaxing Spins with Anisotropic g-Tensors.

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(This is a paper contributed at the ESR2007-40th RSC-COSTP15 meeting Oxford March 2007)

Keywords: Paramagnetic, relaxation enhancement, dipolar interaction, g-anisotropy, EPR.

Abstract

Paramagnetic relaxation enhancement is a fundamental molecular physical phenomenon, manifested as an acceleration of the relaxation times of a slowly relaxing spin $\mathbf{S}^{\mathbf{slow}}$ due to the magnetic interaction, dipolar or exchange, with a fast relaxing spin $\mathbf{S}^{\mathbf{fast}}$. Here, we examine the general case of the enhancement of T_1^{slow} due to a fast relaxer $\mathbf{S}^{\mathbf{fast}}$ with rhombic g-tensor. By using the formalism of Kubo and Tomita we derive the following analytical expression for the dipolar effect on T_1^{slow}.

$$\frac{1}{T_{1,dip}} = \left[\frac{\mu_o}{4\pi}\right]^2 \frac{\mu_B^4}{\hbar^2 R^6} \frac{S^f (S^f+1)(g^s)^2}{3} \times$$
$$\left\{ \begin{array}{l} \dfrac{2T_{1S}}{1+(\omega^s T_{1S})^2}\left[g_3^{\,2} f_0\right] + \\ + \dfrac{2T_{2S}}{1+[(\omega^f(\theta,\phi)-\omega^s)T_{2S}]^2}\left[A^2 f_1 + B^2 f_2 - ABf_3\right] \\ + \dfrac{2T_{2S}}{1+[(\omega^f(\theta,\phi)+\omega^s)T_{2S}]^2}\left[A^2 f_2 + B^2 f_1 - ABf_3\right] \end{array} \right\}$$

where $A \equiv ½(g^f_1+g^f_2)$, $B \equiv ½(g^f_1-g^f_2)$ i.e. B is the g-rhombicity factor and f_0, f_1, f_2, f_3 are angular functions of the angles θ, φ and the Euler angles (β, γ).

1. Introduction

Fast relaxing electron spins can affect the relaxation properties T^s_1 and T^s_2 of nearby slow relaxing, electron [1, 2] or nuclear [3-5] spins. This effect has been originally described by Bloembergen [6] and later by Abragam [7] in an NMR context, and later for the case of EPR by Kulikov and Lichtenshtein [1] and Hyde and Rao [8] for rigid systems where no spatial averaging occurs. There are many theoretical aspects of the literature on NMR that are immediately relevant, most of which have been discussed in Abragam's book [9]. A point of caution however is that many of the equations in the NMR literature are based on the assumption that $\omega\tau(\text{NMR}) \ll 1$, where ω is the radiofrequency and τ the pertinent correlation time. In general in EPR at X-band (~10GHz) or higher frequencies, the inequality is reversed thus $\omega\tau(\text{EPR}) \gg 1$ [2, 9]. The original equations [6, 7] have been derived for isotropic g-tensors for interacting spins with S=1/2. The effect of g-anisotropy on the nuclear relaxation enhancement was first addressed by Sterlincht for the case of an axially symmetric electron g-tensor, under the assumption $\omega\tau \ll 1$ for liquids [11]. Further refinements i.e. effects of zero-field splitting, scalar couplings etc., are discussed by Banci et al. [3] and Sharp et al. [5].

In EPR spectroscopy, the dipolar relaxation enhancement on T^s_1 in rigid systems has been studied extensively by many groups. The fundamental condition for the dipolar-induced electron spin relaxation in solids is that the spin-lattice relaxation time, T^f_1, is equal or greater than the reciprocal of the dipolar interaction between the fast- and slow-relaxing electron spins. In the opposite case lineshape broadening and/or splittings occur in the EPR spectra [2, 10].

During the past decades, the EPR dipolar relaxation enhancement on T^s_1 in rigid systems has been exploited fruitfully for the estimation of the spin-spin distance in biological systems and model compounds. Pertinent reviews of the vast literature, are presented in reference [12]. To name just a few examples, we mention nitroxide spin labels interacting with low spin Fe^{3+} studied in detail by Eaton et. al [13]. Most importantly this method has been applied for distance estimate in complicated biological systems, such as milk Xanthane Oxidase [14], Cytochrome *c* Oxidase [15], Nitrogenase [16] ubiquinone reductase from *Paracoccus Denitrificants* [17], Hydrogenase [18], Spin-Labelled methemoglobin [19] and Ribonucleotide Reductase [20, 21]. In

Photosynthetic reaction centres this method has been proven particularly useful in efforts to map distances in Photosystem II [22-24] and Photosystem I [25] long before any crystal structure become available.

In all the cited cases the expression used for the estimation of the $1/T^s_1$(dipolar) was that developed by Kulikov and Likhtenstein [1] and Hyde et al., [2, 8], which is valid for isotropic g-tensors for the slow as well as for the fast relaxing electron spins, based on the original works [1, 2, 8]. No expression for $1/T^s_1$(dipolar) is available for the general case where the fast relaxer has an anisotropic g-tensor. Due to this lack the usual practice was to use an average g-value in the expression of Kulikov and Lichtenshtein. More recently, the effect of an anisotropic exchange term in conjunction with the g-anisotropy has been discussed in some detail by the groups of Britt and Chan [17]. This work provided numerical solutions of the pertinent equations in graphical form, and consists a significant advancement towards a more complete description of the dipolar relaxation enhancement on T^s_1 in rigid systems. However an analytical expression for the $1/T^s_1$(dipolar) in the general case has not been derived.

In the present work an analytical solution for the paramagnetic dipolar relaxation enhancement on T^s_1 in rigid systems is derived for the general case of a rhombic g-tensor of the fast relaxer. In terms of a practical implication the present work highlights representative cases on the effects of the g-anisotropy on the estimation of the interspin distance. This bears relevance to practical problems of distance estimate based on dipolar relaxation enhancement on T^s_1. An analytical expression for T^s_2 can be straightforwardly derived based on the present approach, however, for space reasons, it is out of the scope of the present paper. The case for T^s_2 will be discussed in detail in a forthcoming publication.

2. Theoretical

The Kubo-Tomita [26] description of spin relaxation leads to the following equation for the enhancement of the relaxation rate of a slow-relaxing electron spin $\boldsymbol{S}^S$ caused by dipolar coupling with a fast-relaxing electron spin $\boldsymbol{S}^f$:

$$\frac{1}{T_{1,dip}} = \frac{1}{\hbar^2}\sum_{k=-1}^{1}\int_0^{\infty}\left\langle\left[S_Z^S, H_{dip}^k(t)\right]\left[H_{dip}^{-k}(0), S_Z^S\right]\right\rangle \frac{e^{(ik\omega_s t)}}{\left\langle (S_Z^S)^2\right\rangle}dt \qquad (1)$$

where the spin-Hamiltonian for the dipolar interaction is

$$H_{dip}^k = A(-1)^{1-k} S_k^{s(1)} F_{-k}^{(1)} \qquad (2)$$

In relations (1) and (2) $S_k^{s(1)}$, k= -1, 0, 1, are the three components of the first-rank tensor

$$S_{+1}^{s(1)} = -\frac{1}{\sqrt{2}} S_{+1}^s, \qquad (3a)$$

$$S_{\grave{a}}^{s(1)} = S_Z^s, \qquad (3b)$$

$$S_{-1}^{s(1)} = +\frac{1}{\sqrt{2}} S_{-1}^s \qquad (3c)$$

and, in S.I. units

$$\Delta = -\frac{\mu_0}{4\pi}\frac{\sqrt{10}\gamma_s\beta\hbar}{R^3} = -\frac{\mu_0}{4\pi}\frac{\sqrt{10}g_s\beta^2}{R^3} \qquad (4)$$

g_s is the g-factor of the slow-relaxing electron spin, which is considered to be isotropic. β is the Bohr magneton for the electron μ_o is the permeability of the vacuum and R is the distance between the spins S^s and S^f. Hereafter we use the index s to denote quantities referring to the

slow relaxing spin, i.e. the 'relaxee', and index f to denote quantities referring to the fast relaxing spin , i.e. the 'relaxer'.

The components of the first-rank tensor $\mathbf{F^{(1)}}$ are constructed by contracting the tensors $\mathbf{G^{(1)}}$ and $\mathbf{C^{(2)}}$ [3, 4, 27]

$$\mathbf{F^{(1)}} = \{\mathbf{G^{(1)}} \otimes \mathbf{C^{(2)}}\}^{(1)} \tag{5}$$

where $\mathbf{G^{(1)}}$ is the spherical first-rank tensor obtained as the product of the vector $\boldsymbol{S}^f$ and the rhombic g-tensor, $\mathbf{g}^{\mathrm{f}}$, of the fast-relaxing electron spin, which is considered to be part of the 'lattice'. When written in its principal axis system (PAS) the $\mathbf{g}^{\mathrm{f}}$ tensor, is

$$\mathbf{g}^{\mathrm{f}} = \begin{bmatrix} g_1 & & \\ & g_2 & \\ & & g_3 \end{bmatrix} \tag{6}$$

and, in the same system, the components of $\mathbf{G^{(1)}}$ are

$$G^{(1)}_{+1} = \frac{(g_1 + g_2)}{2} S^{f(1)}_{+1} + \frac{(g_2 - g_1)}{2} S^{f(1)}_{-1} \tag{7a}$$

$$G^{(1)}_{0} = g_3 S^{f(1)}_{0} \tag{7b}$$

$$G^{(1)}_{-1} = \frac{(g_1 - g_2)}{2} S^{f(1)}_{+1} + \frac{(g_1 + g_3)}{2} S^{f(1)}_{-1} \tag{7c}$$

where

$$S^{f(1)}_{+1} = -\frac{1}{\sqrt{2}} S^{f}_{+1} = -\frac{1}{\sqrt{2}} \left(\frac{S^f_X + S^f_Y}{2} \right), \tag{8a}$$

$$S^{f(1)}_{0} = S^f_Z \,, \tag{8b}$$

$$S^{f(1)}_{-1} = \frac{1}{\sqrt{2}} S^{f}_{-1} = \frac{1}{\sqrt{2}} \left(\frac{S^f_X - S^f_Y}{2} \right) \tag{8c}$$

In equation (5) $\mathbf{C}^{(2)}$ is the second-rank tensor formed by the polar variables (θ, ϕ) given by the Racah's normalised spherical harmonics [27, 28]

$$C_q^{(2)}(\theta,\phi) = \sqrt{\frac{4\pi}{5}}\, Y_q^2(\theta,\phi) \qquad (9)$$

where $Y_q^2(\theta,\phi)$ are spherical harmonics of second order. Here (θ, ϕ) specify the orientation of the interspin vector $\boldsymbol{S}^s$-$\boldsymbol{S}^f$ in the laboratory frame where the external magnetic field $\boldsymbol{B}_0$ defines the z axis, see Figure 1.

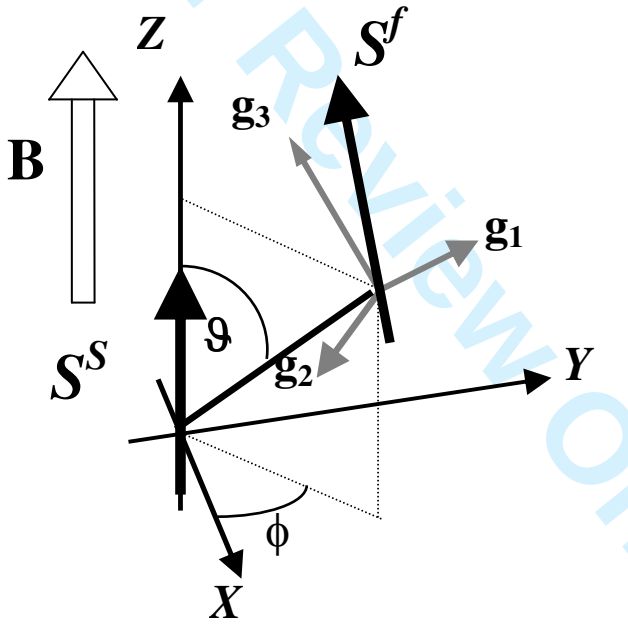

FIGURE 1: Reference axes systems

Thus, by combining (7a-c), (8a-c) and (9) the components of $\mathbf{F}^{(1)}$ are given by

$$F_m^{(1)} = \sum_{l=-1}^{1} \sum_{n=-2}^{1} (-1)^{1-n} \sqrt{3} \begin{pmatrix} 1 & 2 & 1 \\ l & n & m \end{pmatrix} S_l^{f\,(1)} C_n^{(2)}(\theta, \phi) \qquad (10)$$

where $S_l^{f\,(1)}$ are the components of the first-rank tensor composed of the spin variables of the fast-relaxinf spin $\boldsymbol{S}^f$, given in equations (8) and $C_n^{(2)}(\theta, \phi)$ are given in expression (9). The pertinent 3-*j* symbols are taken from reference [28].

The form of $\mathbf{F}^{(1)}$ in (5) implies that the fast-relaxing spin $\boldsymbol{S}^f$ forms part of the 'lattice' undergoing time-dependent fluctuations. In paramagnetic systems in frozen solutions, which is typical for EPR samples, the time dependence of $\mathbf{F}^{(1)}$ originates exclusively from the motion of the fast-relaxing electron spin $\boldsymbol{S}^f$. In rigid systems, e.g. frozen solutions or solids, the polar coordinate factors do not fluctuate, in contrast to the NMR case is solution.

Evaluating the 3-*j* symbols, in equation (10) gives the following form for the components of $\mathbf{F}^{(1)}$.

$$F_m^{(1)} = \sqrt{\frac{4\pi}{5}} \sum_{l=-1}^{1} c_{m,l}\, G_l^{(1)}\, Y_{m-l}^{(2)}(\theta, \phi) \qquad (11a)$$

where the factors $c_{m,j}$ are [4, 27]

$$\begin{array}{cccc} C_{m,l} & +1 & 0 & -1 \\ +1 & +\frac{1}{\sqrt{2}} & -\frac{\sqrt{3}}{\sqrt{10}} & \frac{\sqrt{3}}{\sqrt{5}} \\ 0 & +\frac{\sqrt{3}}{\sqrt{10}} & -\frac{\sqrt{2}}{\sqrt{5}} & +\frac{\sqrt{3}}{\sqrt{10}} \\ -1 & \frac{\sqrt{3}}{\sqrt{5}} & -\frac{\sqrt{3}}{\sqrt{10}} & +\frac{1}{\sqrt{2}} \end{array} \qquad (11b)$$

Combining equations (11a) and (11b) the explicit form of the $F_m^{(1)}$ components is

$$F_{+1}^{(1)} = \sqrt{\frac{3}{10}}\, G_{-1}^{(1)} Y_{+2}^{(2)} - \sqrt{\frac{3}{10}}\, G_{0}^{(1)} Y_{+1}^{(2)} - \sqrt{\frac{3}{10}}\, G_{+1}^{(1)} Y_{0}^{(2)} \qquad (12a)$$

$$F_{0}^{(1)} = \sqrt{\frac{3}{20}}\, G_{-1}^{(1)} Y_{-1}^{(2)} - \sqrt{\frac{2}{5}}\, G_{0}^{(1)} Y_{0}^{(2)} - \sqrt{\frac{3}{20}}\, G_{+1}^{(1)} Y_{-1}^{(2)} \qquad (12b)$$

$$F_{-1}^{(1)} = \sqrt{\frac{3}{20}}\, G_{-1}^{(1)} Y_{0}^{(2)} - \sqrt{\frac{3}{10}}\, G_{0}^{(1)} Y_{-1}^{(2)} - \sqrt{\frac{3}{10}}\, G_{+1}^{(1)} Y_{-2}^{(2)} \qquad (12c)$$

Then by using (2) and (12a-c) for the dipolar interaction, the correlation functions in the Kubo-Tomita equation (1) become,

$$\left\langle \left[S_Z^S, H_{dip}^{k}(t) \right] \left[H_{dip}^{-k}(0), S_Z^S \right] \right\rangle = \Delta^2 \left\langle \left(S_Z^S \right)^2 \right\rangle \left\langle (-1)^k k F_k^{(1)}(t)\, F_{-k}^{(1)}(0) \right\rangle =$$

$$= \Delta^2 \frac{S^s(S^s+1)}{3} (-1)^k k \left\langle F_k^{(1)}(t)\, F_{-k}^{(1)}(0) \right\rangle \qquad (13)$$

The dipole-dipole paramagnetic relaxation enhancement of T_1 of the slow-relaxing spin S^s is

$$\frac{1}{T_{1,dip}} = \frac{1}{\hbar^2} \frac{\Delta^2}{\left\langle (S_Z^S)^2 \right\rangle} \frac{S^s(S^s+1)}{3} \int_0^\infty \left\langle F_{+1}^{(1)}(t), F_{-1}^{(1)}(0) \right\rangle e^{-ik\omega_s t} dt + \left\langle F_{-1}^{(1)}(t), F_{+1}^{(1)}(0) \right\rangle e^{+ik\omega_s t} dt \qquad (14)$$

Equation (14) is the starting point for the evaluation of longitudinal-relaxation-rate enhancement in magnetic resonance. This equation is written assuming that the $\boldsymbol{S^s}$ vector is quantized along the external magnetic field $\boldsymbol{B_0}$, i.e. along the z axis in the laboratory frame. Therefore in (14) the components of $F^{(1)}$ are written in the laboratory coordinate frame.

For the evaluation of the longitudinal-relaxation-rate enhancement in equation (14) we need to evaluate the functions $\left\langle F_{+1}^{(1)}(t), F_{-1}^{(1)}(0)\right\rangle$ and $\left\langle F_{-1}^{(1)}(t), F_{+1}^{(1)}(0)\right\rangle$. Ultimately, as it is shown below, we have to calculate the correlation functions of the spin operators of the fast-relaxing-spin $\boldsymbol{S}^f$. In the present case these correlation function are calculated in the coordinate system where the $\mathbf{g}^{\mathbf{f}}$-tensor is diagonal. In the general case when $\mathbf{g}^{\mathbf{f}}$ is rhombic, the spin $\boldsymbol{S}^f$ is quantized in that system undergoing its precessional motion with respect to the unit vector defined by

$$\vec{\mathbf{u}} = \frac{\mathbf{g}^{\mathbf{f}}\mathbf{B}_0}{\left|\mathbf{g}^{\mathbf{f}} \bullet \mathbf{B}_0\right|} = \frac{\mathbf{g}^{\mathbf{f}}}{\left|\mathbf{g}^{\mathbf{f}}\right|}\vec{\mathbf{l}} \qquad (15)$$

where $\vec{\mathbf{l}}$ is the unit vector along the direction of the external magnetic field $\mathbf{B}_0$ in the laboratory frame. From (15) is seen that in general the direction of $\vec{\mathbf{u}}$ does not coincide with the direction of $\mathbf{B}_0$. Only in cases when $\mathbf{B}_0$ is along a given principal axes of the $\mathbf{g}^{\mathbf{f}}$-tensor, then the direction of the unit vector $\vec{\mathbf{u}}$ is along this principal axes.

The components of $F^{(1)}$ can be written in the coordinate frame of the $\mathbf{g}^{\mathbf{f}}$-tensor by use of the Wigner rotation matrices $D^{(1)}(\alpha\beta\gamma)$ [table 2.12 from reference 27],

$$D^{(1)}(\alpha\beta\gamma) = \begin{pmatrix} e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)e^{i\gamma} & e^{i\gamma}\left(\frac{\sin\beta}{\sqrt{2}}\right) & e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)e^{-i\alpha} \\ -e^{i\alpha}\left(\frac{\sin\beta}{\sqrt{2}}\right) & \cos\beta & e^{-i\alpha}\left(\frac{\sin\beta}{\sqrt{2}}\right) \\ e^{i\alpha}\left(\frac{1-\cos\beta}{2}\right)e^{-i\gamma} & -e^{-i\gamma}\left(\frac{\sin\beta}{\sqrt{2}}\right) & e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)e^{-i\gamma} \end{pmatrix} \qquad (16a)$$

we have

$$F_k^{(1)} = D_{+1k}^{(1)}(\alpha\beta\gamma)\,\hat{F}_{+1}^{(1)} + D_{0k}^{(1)}(\alpha\beta\gamma)\,\hat{F}_{0}^{(1)} + D_{-1k}^{(1)}(\alpha\beta\gamma)\,\hat{F}_{-1}^{(1)} \qquad \text{for } k = -1,\ 0,\ 1 \qquad (16b)$$

where α, β, γ are the Euler angles which effect the transformation of the coordination axes

([laboratory axes system]→[principal axes system of $\mathbf{g}^{\mathbf{f}}$])

In the following, the Euler angles α, β, γ (which are the arguments of the Wigner transformation matrix) and the polar angles θ, ϕ (which are the arguments of the spherical harmonics) are omitted for the shake of brevity.

Herein, operators written in the principal axes system of $\mathbf{g}^{\mathbf{f}}$ -tensor display a superscript caret ; those in the laboratory frame do not. For compatibility our notation here parallels that used in the literature describing paramagnetic relaxation enhancement in NMR [3-5], with the nuclear spin symbol $\boldsymbol{I}$ replaced by $\boldsymbol{S}^{s}$.

After transforming components of $F^{(1)}$ according to (16), the correlation functions in (14) become

$$\left\langle F^{(1)}_{+1}(t), F^{(1)}_{-1}(0)\right\rangle =$$

$$\begin{aligned}
&\left\langle \hat{F}^{(1)}_{+1}(t)\hat{F}^{(1)}_{+1}(0)\right\rangle D^{(1)}_{11} D^{(1)}_{1-1} + \left\langle \hat{F}^{(1)}_{+1}(t)\hat{F}^{(1)}_{0}(0)\right\rangle D^{(1)}_{11} D^{(1)}_{0-1} + \left\langle \hat{F}^{(1)}_{+1}(t)\hat{F}^{(1)}_{-1}(0)\right\rangle D^{(1)}_{11} D^{(1)}_{-1-1} + \\
&\left\langle \hat{F}^{(1)}_{0}(t)\hat{F}^{(1)}_{+1}(0)\right\rangle D^{(1)}_{01} D^{(1)}_{1-1} + \left\langle \hat{F}^{(1)}_{0}(t)\hat{F}^{(1)}_{0}(0)\right\rangle D^{(1)}_{01} D^{(1)}_{0-1} + \left\langle \hat{F}^{(1)}_{0}(t)\hat{F}^{(1)}_{-1}(0)\right\rangle D^{(1)}_{01} D^{(1)}_{-1-1} + \\
&\left\langle \hat{F}^{(1)}_{-1}(t)\hat{F}^{(1)}_{+1}(0)\right\rangle D^{(1)}_{-11} D^{(1)}_{1-1} + \left\langle \hat{F}^{(1)}_{-1}(t)\hat{F}^{(1)}_{0}(0)\right\rangle D^{(1)}_{-11} D^{(1)}_{0-1} + \left\langle \hat{F}^{(1)}_{-1}(t)\hat{F}^{(1)}_{-1}(0)\right\rangle D^{(1)}_{-11} D^{(1)}_{-1-1}
\end{aligned} \qquad (17a)$$

in a similar manner we may write the expression for $\left\langle F^{(1)}_{-1}(t), F^{(1)}_{+1}(0)\right\rangle$

$$\left\langle F_{-1}^{(1)}(t), F_{+1}^{(1)}(0)\right\rangle =$$

$$\begin{aligned}
&\left\langle \hat{F}_{+1}^{(1)}(t)\,\hat{F}_{+1}^{(1)}(0)\right\rangle D_{1-1}^{(1)}D_{11}^{(1)} + \left\langle \hat{F}_{+1}^{(1)}(t)\,\hat{F}_{0}^{(1)}(0)\right\rangle D_{1-1}^{(1)}D_{01}^{(1)} + \left\langle \hat{F}_{+1}^{(1)}(t)\,\hat{F}_{-1}^{(1)}(0)\right\rangle D_{1-1}^{(1)}D_{-11}^{(1)} + \\
&\left\langle \hat{F}_{0}^{(1)}(t)\,\hat{F}_{+1}^{(1)}(0)\right\rangle D_{0-1}^{(1)}D_{11}^{(1)} + \left\langle \hat{F}_{0}^{(1)}(t)\,\hat{F}_{0}^{(1)}(0)\right\rangle D_{0-1}^{(1)}D_{01}^{(1)} + \left\langle \hat{F}_{0}^{(1)}(t)\,\hat{F}_{-1}^{(1)}(0)\right\rangle D_{0-1}^{(1)}D_{-11}^{(1)} + \\
&\left\langle \hat{F}_{-1}^{(1)}(t)\,\hat{F}_{+1}^{(1)}(0)\right\rangle D_{-1-1}^{(1)}D_{11}^{(1)} + \left\langle \hat{F}_{-1}^{(1)}(t)\,\hat{F}_{0}^{(1)}(0)\right\rangle D_{-1-1}^{(1)}D_{01}^{(1)} + \left\langle \hat{F}_{-1}^{(1)}(t)\,\hat{F}_{-1}^{(1)}(0)\right\rangle D_{-1-1}^{(1)}D_{-11}^{(1)}
\end{aligned} \tag{17b}$$

We then substitute relations (12) in 17a, 17b, perform the necessary (lengthy although straightforward) calculations, then substitute (7) and finally (14) becomes

$$\begin{aligned}
\frac{1}{T_{1,dip}} = \frac{1}{\hbar^2}\int_0^{\infty}\Bigg\{ &\left\langle \hat{S}_0^f(t)\,\hat{S}_0^f(0)\right\rangle [f_0] + \\
&\left[\left\langle \hat{S}_{+1}^f(t)\,\hat{S}_{-1}^f(0)\right\rangle e^{-ik\omega_s t} + \left\langle \hat{S}_{-1}^f(t)\,\hat{S}_{+1}^f(0)\right\rangle e^{+ik\omega_s t}\right]\left[A^2 f_1 + B^2 f_2 - ABf_3\right] + \\
&\left[\left\langle \hat{S}_{+1}^f(t)\,\hat{S}_{-1}^f(0)\right\rangle e^{+ik\omega_s t} + \left\langle \hat{S}_{-1}^f(t)\,\hat{S}_{+1}^f(0)\right\rangle e^{-ik\omega_s t}\right][A^2 f_1 + B^2 f_2 - ABf_3]\Bigg\} dt
\end{aligned} \tag{18a}$$

where we define

$$A \equiv \tfrac{1}{2}(g^f_1 + g^f_2) \tag{18b}$$

and

$$B \equiv \tfrac{1}{2}(g^f_1 - g^f_2) \tag{18c}$$

i.e. B is the $\mathbf{g}^f$-rhombicity factor.

The functions f_0, f_1, f_2 and f_3 contain all the angular dependent factors. Their explicit form is

$$f_0(\beta,\gamma,\theta,\phi) = \frac{9}{320}\sin^2(2\theta)\sin^2\beta\cos[2(\phi+\gamma)]$$
$$-\frac{12}{320}\left(1-3\cos^2\theta\right)\sin(2\theta)\sin(2\beta)\cos(\phi+\gamma)$$
$$-\frac{16}{320}\left(1-3\cos^2\theta\right)\sin^2\beta \qquad (19a)$$
$$-\frac{18}{320}\sin^2(2\theta)(1+\cos^2\beta)$$

$$f_1(\beta,\gamma,\theta,\phi) = \frac{3}{320}\sin^2\theta\left(3\cos^2\theta-1\right)\sin^2\beta\cos[2(\phi+\gamma)]$$
$$-\frac{3}{320}\left(3\cos^2\theta-1\right)(1+\cos\beta)\sin(2\theta)\sin\beta\cos(\phi+\gamma)$$
$$-\frac{9}{320}\sin^2\theta(1-\cos\beta)\sin(2\theta)\sin\beta\cos(\phi+\gamma) \qquad (19b)$$
$$+\frac{1}{320}\left(3\cos^2\theta-1\right)^2(1+\cos\beta)^2$$
$$+\frac{9}{320}\sin^2(2\theta)\sin^2\beta$$
$$+\frac{9}{320}\sin^4\theta(1-\cos\beta)^2$$

$$f_2(\beta,\gamma,\theta,\phi) = \frac{3}{320}\sin^2\theta\left(3\cos^2\theta-1\right)\sin^2\beta\cos[2(\phi+\gamma)]$$
$$-\frac{3}{320}\left(3\cos^2\theta-1\right)(1-\cos\beta)\sin(2\theta)\sin\beta\cos(\phi+\gamma)$$
$$-\frac{9}{320}\sin^2\theta(1+\cos\beta)\sin(2\theta)\sin\beta\cos(\phi+\gamma) \qquad (19c)$$
$$+\frac{1}{320}\left(3\cos^2\theta-1\right)^2(1-\cos\beta)^2$$
$$+\frac{9}{320}\sin^2(2\theta)\sin^2\beta$$
$$+\frac{9}{320}\sin^4\theta(1+\cos\beta)^2$$

$$
\begin{aligned}
\mathrm{f}_3(\beta,\gamma,\theta,\phi) &= \frac{1}{320}\left(3\cos^2\theta-1\right)\sin^2\beta\cos(2\gamma)\\
&+\frac{9}{320}\sin^4\theta\sin^2\beta\cos[(2(2\phi+\gamma)]\\
&-\frac{9}{320}\sin^2(2\theta)\sin^2\beta\cos(2\phi)\\
&+\frac{3}{320}\left(3\cos^2\theta-1\right)\sin(2\theta)\sin(2\beta)\cos(\phi-\gamma)\\
&+\frac{6}{320}\left(3\cos^2\theta-1\right)\sin^2\theta\cos^2\beta\cos(2\phi)\\
&+\frac{9}{320}\sin(2\theta)\sin^2\theta\sin(2\beta)\cos(3\phi-\gamma)
\end{aligned}
\qquad (19d)
$$

We notice that the angle α is absent in expressions (19a, b, c). This results directly from the form of the products $D^{(1)}{}_{q,\,q'}\,D^{(1)}{}_{m,\,m'}$ in (17a, b).

In the Heisenberg representation the time-dependence of S^f is

$$\hat{S}^f_q(t) = e^{iH^{(0)}t}\hat{S}^f_q(0)e^{-iH^{(0)}t} \qquad (20)$$

$H^{(0)}$ is the static spin-Hamiltonian, which in the $\mathbf{g}^{\mathrm{f}}$-coordinate frame has the form

$$H^{(0)} = \mu_{\mathrm{B}}B_0 g^f(\vartheta,\phi)\hat{S}^{f(1)}_0 \qquad (21)$$

and describes the precessional motion of the spin S^f with respect to the unit vector $\vec{\mathbf{u}}$, see (15), due to Zeeman interaction.

For the evaluation of the spin correlation functions we assume: (a) the high temperature approximation, (b) the time-dependent part of $H^{(0)}$ i.e. that describing the coupling of the spin S^f with the thermal lattice, gives rise to the relaxation of S^f. This is not included in (21) but is taken into account pheonomenologically through the use of the exponential decays describing the effects of the stochastic time dependence of $\hat{S}^f_Z$ and $\hat{S}^f_{\pm}$ having time-constants the longitudinal,

T_{1f} , and transverse, $T_{2f,}$ relaxation times of the fast-relaxing spin respectively. (c) for S^f>½, although different transitions of the fast-relaxing spin may have different relaxation times, common T_{1f} , and T_{2f} are assumed. The validity of this assumption is discussed in the literature [3-5, 9, 28].

Within these assumptions we have

$$\left\langle \hat{S}^f_{\pm 1}(t), \hat{S}^f_{\mp 1}(0) \right\rangle = \left\{ \frac{1}{2S^f + 1} \sum_{m,n} \langle m | \hat{S}^f_{\pm 1}(t) | n \rangle \langle n | \hat{S}^f_{\mp 1}(0) | m \rangle \right\} e^{-\frac{t}{T_{2S}}} \tag{22a}$$

$$\left\langle \hat{S}^f_{0}(t), \hat{S}^f_{0}(0) \right\rangle = \left\{ \frac{1}{2S^f + 1} \sum_{m,\ n} \langle m | \hat{S}^f_{0}(t) | n \rangle \langle n | \hat{S}^f_{0}(0) | m \rangle \right\} e^{-\frac{t}{T_{1S}}} \tag{22b}$$

where $|m\rangle$ and $|n\rangle$ are eigenvectors of $H^{(0)}$. In this basis, the matrix elements of $\hat{S}^f_Z$ and $\hat{S}^f_{\pm}$ can be written

$$\langle n | \hat{S}^f_0(t) | m \rangle = \langle n | \hat{S}^f_0(0) | m \rangle \tag{23a}$$

and

$$\langle n | \hat{S}^f_{\pm}(t) | m \rangle = \langle n | \hat{S}^f_{\pm}(0) | m \rangle e^{i(\omega_n - \omega_m)t} \tag{23b}$$

where ω_n and ω_m are the eigenvalues of $H^{(0)}$ associated with $|m\rangle$ and $|n\rangle$.

Combining relations (23) with (22) we have

$$\left\langle \hat{S}^f_{\pm 1}(t), \hat{S}^f_{\mp 1}(0) \right\rangle = 2 \frac{S^f (S^f + 1)}{3} e^{i(\omega_f \mp \frac{1}{T_{2S}})t} \tag{24a}$$

$$\left\langle \hat{S}^f_{0}(t), \hat{S}^f_{0}(0) \right\rangle = \frac{S^f (S^f + 1)}{3} e^{-i(\frac{1}{T_{1S}})t} \tag{24b}$$

where

$$\omega_f \equiv \omega_n - \omega_m$$

is the transition energy of the fast-relaxing spin

$$\omega^f(\theta,\phi)=\frac{1}{\hbar}\mathrm{B}_o\beta g^f(\theta,\phi)$$

which introduces the anisotropy of the resonance energies for the fast relaxing spin.

Substituting (24a-b) in (18a), and integrating over time gives the final result

$$\frac{1}{T_{1,dip}}=\left[\frac{\mu_o}{4\pi}\right]^2\frac{\beta^4}{\hbar^2R^6}\frac{S^f(S^f+1)(g^s)^2}{3}\times$$
$$\left\{\begin{array}{l}\dfrac{2T_{1S}}{1+(\omega^sT_{1S})^2}\left[g_3{}^2f_0\right]+\\ +\dfrac{2T_{2S}}{1+[(\omega^f(\theta,\phi)-\omega^s)T_{2S}]^2}\left[A^2f_1+B^2f_2-ABf_3\right]\\ +\dfrac{2T_{2S}}{1+[(\omega^f(\theta,\phi)+\omega^s)T_{2S}]^2}\left[A^2f_2+B^2f_1-ABf_3\right]\end{array}\right\} \qquad (25)$$

where $\omega^f(\theta,\phi)=\frac{1}{\hbar}\mathrm{B}_o\beta g^f(\theta,\phi)$

and A, B, f_0, f_1, f_2 , f_3 are defined in equations 19a-d.

3. Discussion

Equation (25) is the main result of this analysis. For the sake of completeness we examine here some characteristic cases.

The structure of relation (25) implies that the $1/T_{1dipolar}$ will be determined by the angular dependent terms f_0, f_1, f_2 , f_3 and the spectral densities

$$J(\omega^s) = \frac{T_{1S}}{1+(\omega^s T_{1S})^2}$$

$$J(\omega^f(\theta,\phi)-\omega^s) = \frac{T_{2S}}{1+[(\omega^f(\theta,\phi)-\omega^s)T_{2S}]^2} \qquad (26)$$

$$J(\omega^f(\theta,\phi)+\omega^s) = \frac{T_{2S}}{1+[(\omega^f(\theta,\phi)+\omega^s)T_{2S}]^2}$$

which are also angle i.e. θ, φ, dependent through the angular dependence of the transition frequency ω^f of the fast relaxing spin.

In the following, the relative importance of these terms will be discussed quantitatively through the investigation of representative cases. To keep things at a concise level, all the calculations have been carried out for one set of T^f_1, T^f_2 and R values i.e. T^f_1 =100ns, T^f_2=10ns and R=10Å. The value ω^s was 5.89x 10^{10} Hz (v = 9.4 GHz**).** The choice of the particular values do not harm the validity of the conclusions and observations made here. Other values can be tested straight forwardly by using expression (25).

a) Axial g^f-tensor: In the case of an axial g^f-tensor with

$$g_1 = g_2 = g_\perp \text{ and } g_3 = g_\parallel,$$

we have $A = g_\perp$ and zero rhombicitry B=0.

Then we may set

$$\phi=0^o, \gamma=0^o$$

therefore equation (25) becomes

$$\frac{1}{T_{1,dip}} = \left[\frac{\mu_o}{4\pi}\right]^2 \frac{\beta^4 S^f (S^f+1)(g^s)^2}{\hbar^2 R^6} \times$$

$$\left\{ g_{\parallel}^2 \frac{T_{1S}}{1+(\omega^s T_{1S})^2}\left[\frac{1}{6}(3\cos^2\theta-1)^2\sin^2\beta+\frac{3}{8}\sin^2 2\theta(1+\cos^2\beta)\right]+ \right.$$

$$\left. g_{\perp}^2\left[\frac{T_{2S}}{1+[(\omega^f(\theta)-\omega^s)T_{2S}]^2}\left[\frac{1}{6}(3\cos^2\theta-1)^2\left(\frac{1+\cos\beta}{2}\right)^2+\frac{3}{4}\sin^2 2\theta\sin^2\beta+\frac{3}{2}\sin^4\theta\left(\frac{1-\cos\beta}{2}\right)^2\right]\right.\right.$$

$$\left.\left.+\frac{T_{2S}}{1+[(\omega^f(\theta)+\omega^s)T_{2S}]^2}\left[\frac{1}{6}(3\cos^2\theta-1)^2\left(\frac{1-\cos\beta}{2}\right)^2+\frac{3}{4}\sin^2 2\theta\sin^2\beta+\frac{3}{2}\sin^4\theta\left(\frac{1+\cos\beta}{2}\right)^2\right]\right]\right\}$$

(27)

In Figure 2 we display representative calculations for the dipolar relaxation enhancement $1/T_{1dipolar,}$ the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$ and the angular functions f_0, f_1, f_2 and f_3 for an axially symmetric tensor $\boldsymbol{g}^{\mathbf{f}}$ = [3.0, 3.0, 2.0] for $\beta=0^0$. In the case of $\beta=0^0$ there is no dependence on the angle φ. A close inspection of Figure 2 shows that the profile of $1/T_{1dipolar}$ is determined by the profile of $J(\omega_f - \omega_s)$ and the angular factor f_2.

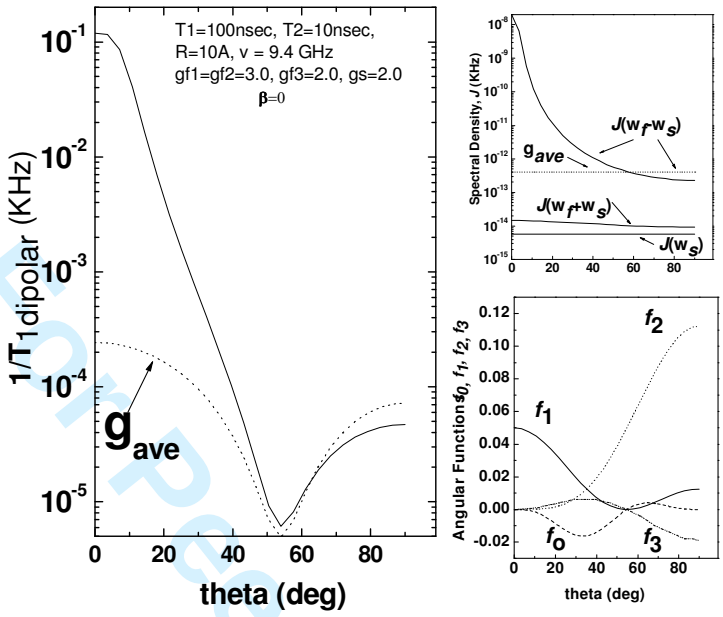

FIGURE 2. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\boldsymbol{g}^{\mathbf{f}}$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ, see Figure 1 for definition. The curves for various angles φ coincide. Calculation parameters g^f = [3.0, 3.0, 2.0], $\beta=0^0$, T_{1fast}=100nsec, T_{2fast}=10nsec, v_{slow} =9.4 GHz, interspin distance R=10Å. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}$= $[g^f_1+g^f_2+g^f_3]/3$=2.67. (Right) Angular dependence of the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$ (upper panel), and f_0, f_1, f_2 and f_3 (lower panel).

However, in general the effect of $J(\omega_f - \omega_s)$ is what determines the angular dependence profile of $1/T_{1dipolar}$. This can be more clearly seen in Figures 3 and 4, for $\beta=30^0$ and $\beta=90^0$ respectively. In all cases the other spectral density terms, $J(\omega_f + \omega_s)$ and $J(\omega_s)$, contribute to a less significant degree than $J(\omega_f-\omega_s)$, see Figures 2, 3 and 4. In addition, angle φ becomes important for $\beta>0^0$. At $\beta=90^0$ the effect of angle φ is maximal for theta angles near 90^0.

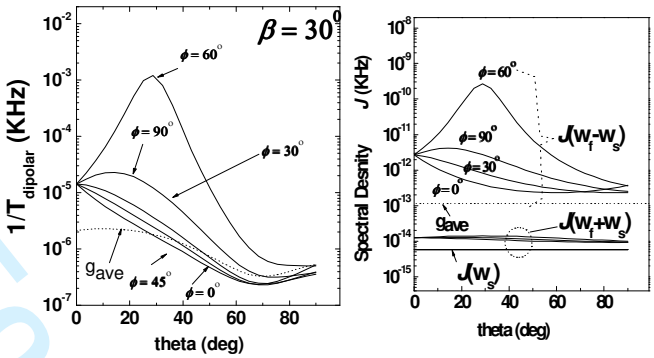

FIGURE 3. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\boldsymbol{g}^{\mathbf{f}}$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ. Calculation parameters $\beta=30^0$, other parameters as in Figure 2. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}= [g^f_1+g^f_2+g^f_3]/3=2.67$. (Right) Angular dependence of the spectral density factors $J(\omega^s)$, $J(\omega^f \pm \omega^s)$.

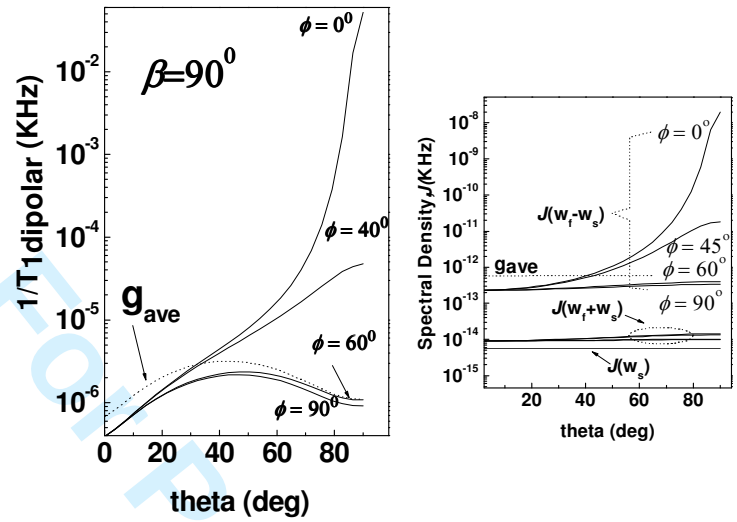

FIGURE 4. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\boldsymbol{g}^{\mathbf{f}}$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ. Calculation parameters $\beta=90^0$, other parameters as in Figure 2. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}= [g^f_1+g^f_2+g^f_3]/3=2.67$. (Right) Angular dependence of the spectral density factors $J(\omega^s)$, $J(\omega^f \pm \omega^s)$.

In Figures 2, 3 and 4 we have superimposed for comparison the $1/T_{1dipolar}$ values calculated by (25) assuming an isotropic g^f value equal to the numerical average of the principal values of the $\mathbf{g}^{\mathbf{f}}$, see dashed lines in Figures 2, 3, 4. This comparison can be helpful for the cases where one uses the average g-value instead of the exact principal g^f-values. This is a practical approach, adopted in the past by many researchers including ourselves [25]. We observe that in certain cases the $1/T_{1dipolar}(g_{ave})$ do not deviate by much from the exact $1/T_{1dipolar}$ i.e. for certain angles θ, φ depending on β.

Probably one of the most important issue with regard to the numerical values of $1/T_{1dipolar}$ is the interspin distance estimate [2, 8, 12]. In saturation recovery experiments on powder EPR

spectra the analysis of the experimental recovery of the magnetization usually involves integration over θ of recovery curves weighted by the factor $\sin\theta$ [12-24]. The $\sin\theta$ term will diminish terms with contribution from $1/T_{1dipolar}$ for $\theta \rightarrow 0^0$ while terms originating from $\theta \rightarrow 90^0$ would be fully accounted for i.e. since $\sin\theta \rightarrow 1$ for $\theta \rightarrow 90^0$. This means that the deviations observed between $1/T_{1dipolar}$(using g_{ave}) *vs* $1/T_{1dipolar}$(using $\mathbf{g}^{\mathbf{f}}$) will be minimal in cases of $\beta << 90^0$ see Figures 2, 3. On the other hand in cases of $\beta \rightarrow 90^0$ the deviation might be considerable, see Figure 4.

This analysis shows that for axial g^f-tensors distance estimates based on $1/T_{1dipolar}$(using g_{ave}) can be made with caution. For an estimate of the error the value of angle β is required. This might be possible, for example by EPR experiments in oriented samples such as biological membranes.

(b) Isotropic g^f-tensor: In the case of isotropic g^f , we may set

$$g_1 = g_2 = g_3 = g^f$$

thus $$A = g^f, \quad B = 0$$

$$\beta = \gamma = 0^o \text{ and } \phi = 0^o$$

Therefore in the angular functions reduce to

$$f_0 = \left[\frac{9}{8}\sin^2 2\theta\right], \quad f_1 = \left[\frac{1}{4}(3\cos^2\theta - 1)^2\right] \text{ and } f_2 = \left[\frac{9}{4}\sin^4\theta\right]$$

therefore (25) gives

$$\frac{1}{T_{1,dip}} = \left[\frac{\mu_o}{4\pi}\right]^2 \frac{\beta^4 S^f (S^f+1)(g^s)^2 (g^f)^2}{\hbar^2 R^6} \times$$
$$\left\{ \frac{T_{1S}}{1+(\omega^s T_{1S})^2}\left[\frac{3}{4}\sin^2 2\theta\right] + \frac{T_{2S}}{1+[(\omega^f-\omega^s)T_{2S}]^2}\left[\frac{1}{6}(3\cos^2\theta-1)^2\right] + \frac{T_{2S}}{1+[(\omega^f+\omega^s)T_{2S}]^2}\left[\frac{3}{2}\sin^4\theta\right]\right\}$$

(28)

Formula (28) is that originally derived for an isotropic g^f by Kulikov and Lichtenshtein [1] which was an adapted version of the original formula derived earlier by Abragam [7] for the NMR case. Calculated $1/T_{1dipolar}$, spectral densities J and angular functions f are those presented in Figure 2 for g_{ave}.

(c) Rhombic $\mathbf{g^f}$ In Figure 5 we display representative calculations for the dipolar relaxation enhancement $1/T_{1dipolar,}$ the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$ for a rhombic tensor $\boldsymbol{g^f}$ = [3.5, 2.5, 2.0]. In contrast to the case of an axial $\mathbf{g^f}$ tensor, a rhombic $\mathbf{g^f}$ tensor causes a dependence $1/T_{1dipolar}$ on the angle φ even in the case of $\beta=0^0$, e.g. compare Figures 2 and 5. As in the case of an axial $\mathbf{g^f}$ tensor the profile of $1/T_{1dipolar}$ is determined by the profile of $J(\omega_f - \omega_s)$ and the angular factor f_2. However in general the effect of $J(\omega_f - \omega_s)$ is more determinative on the profile of $1/T_{1dipolar.}$

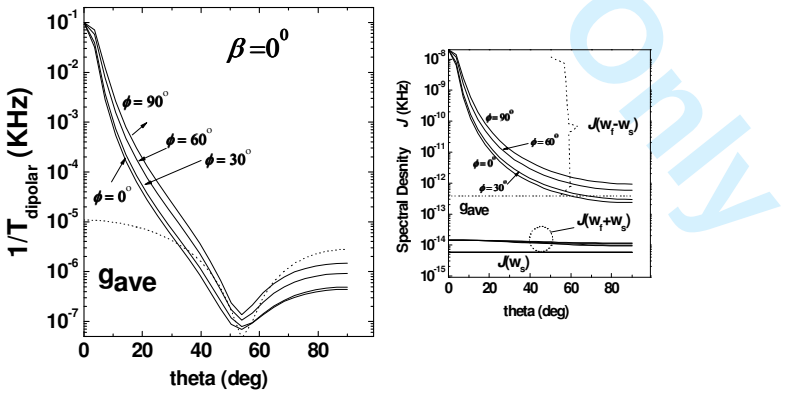

FIGURE 5. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with a rhombic $\boldsymbol{g^f}$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ, see Figure 1 for

definition. Calculation parameters g^f = [3.5, 2.5, 2.0], β=0^0, T_{1fast}=100nsec, T_{2fast}=10nsec, v_{slow} = 9.40GHz, interspin distance R=10Å. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}$= $[g^f_1+g^f_2+g^f_3]/3$=2.67. (Right) Angular dependence of the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$.

This can be more clearly seen in Figures 6 and 7 for β=30^0 and β=90^0 respectively. For both the axial or the rhombic $\mathbf{g}^f$-tensor the other spectral density terms $J(\omega_f+\omega_s)$ and $J(\omega_s)$ contribute to a less significant degree that $J(\omega_f-\omega_s)$, compare Figures 2-4 and 5-7.

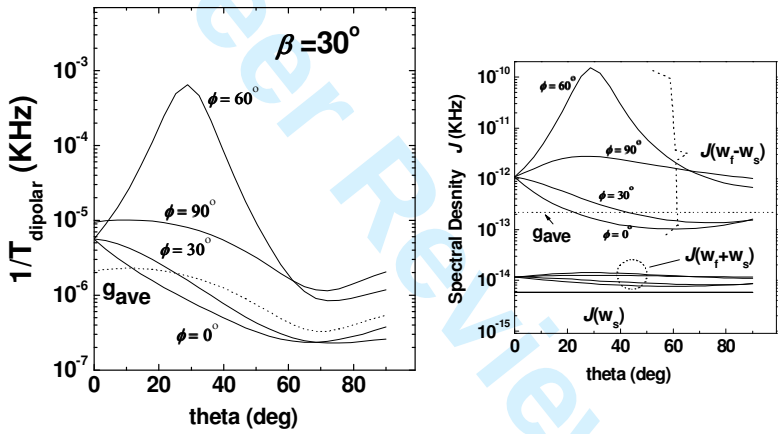

FIGURE 6. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\boldsymbol{g}^f$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ. Calculation parameters β=30^0, other parameters as in Figure 5. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}$= $[g^f_1+g^f_2+g^f_3]/3$=2.67. (Right) Angular dependence of the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$.

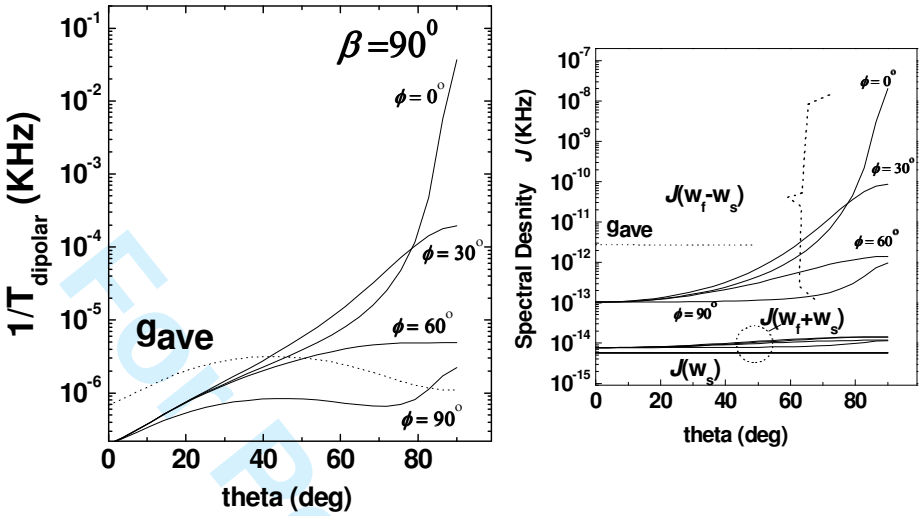

FIGURE 7. (Left) Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\boldsymbol{g}^{\mathbf{f}}$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ. Calculation parameters $\beta=90^0$, other parameters as in Figure 5. The dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}= [g^f_1+g^f_2+g^f_3]/3=2.67$. (Right) Angular dependence of the spectral density factors $J(\omega_s)$, $J(\omega_f \pm \omega_s)$.

Depending on the orientation of the $\mathbf{g}^{\mathbf{f}}$-tensor, the $T^{-1}_{dipolar}$ might deviate significantly from the $T^{-1}_{dipolar}$ estimated by using $g_{average}$, see dashed lines in Figures 5-7. In powder EPR spectra the spatial orientation weighting term, $\sin\theta$, will magnify deviations at θ angles approaching 90^0. On the other hand, deviations occurring for θ angles approaching 0^0 will have minimal effect on the $T^{-1}_{dipolar}$. In Figures 5, 6, 7 this effect is exemplified for $\beta=0^0$, 30^0 and 90^0 respectively. We see that for $\beta=0^0$ or 30^0 the $T^{-1}_{dipolar}(g_{average})$, dashed line in Figure 5, is approaching the $T^{-1}_{dipolar}(\mathbf{g}_f)$, for $\theta > 60^0$. On the other hand for $\beta \rightarrow 90^0$ the values $T^{-1}_{dipolar}(g_{average})$ deviate significantly from $T^{-1}_{dipolar}(\mathbf{g}_f)$, for $\theta > 60^0$, Figure 7. In real experiments this observation implies that for g_{f1}, g_{f2}, $g_{f3} > g_s$ for $\beta \rightarrow 90^0$ the approximative values of $T^{-1}_{dipolar}(g_{average})$ will be *lower* than the real $T^{-1}_{dipolar}(\mathbf{g}_f)$ values. This in turn means, that in cases of distance estimate from $T^{-1}_{dipolar}$ the calculated distance will be *overestimated* if one uses the $g_{average}$ instead of $\mathbf{g}_f$.

(*d*) *g^f_i component lower than g^s* [$g^f_i < g^s$]. The existence of g^f_i values lower than the g^s affects significantly the spectral density functions's angular dependence as well as the $1/T_{1dipolar}(\mathbf{g}^f)$. This is exemplified in Figure 8.

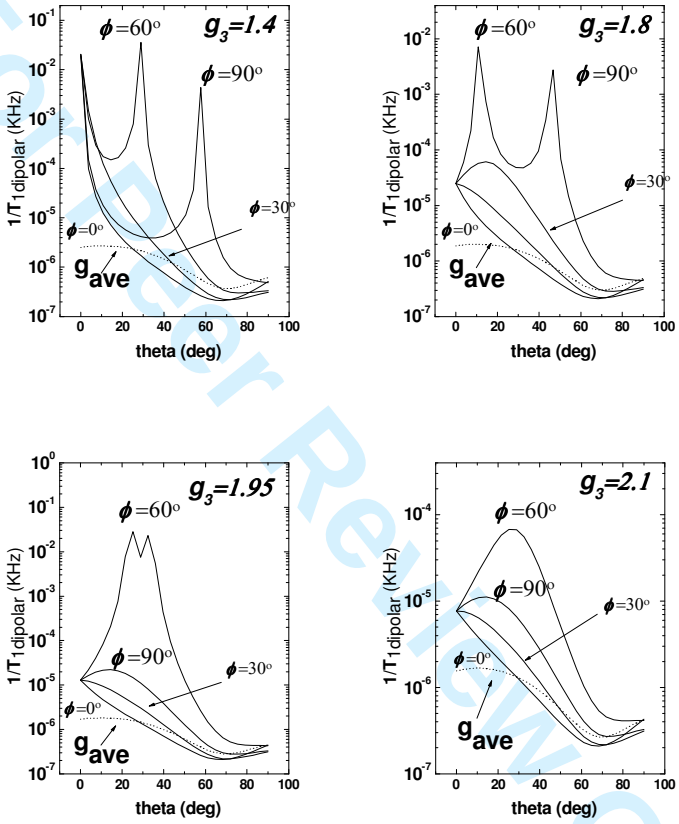

FIGURE 8. Theoretical dipolar relaxation enhancement $1/T_{1dipolar}$ calculated by using expression (25), for a fast relaxing spin with an axial $\mathbf{g}^f$ tensor coupled to a slow relaxing spin with isotropic g^s =2.0 (solid line) as a function of the polar angles θ and φ. Calculation parameters g^f_1=3.2, g^f_2=3.2, g^f_3 varies as indicated, $\beta=30^0$, other parameters as in Figure 5. In each panel the dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}= [g^f_1+g^f_2+g^f_3]/3$.

In Figure 8, we notice that (a) for an increasing g^f_3 - g^s difference the angular dependence of $1/T_{1dipolar}$ shows multiple peaks whose exact position depends on the value of g^f_3 . (b) the T^-

$^{1}_{dipolar}(g_{average})$ might become larger than $T^{-1}_{dipolar}(\mathbf{g}^{f})$. When this occurs for $\theta > 60^{0}$ the spatial orientation weighting term, $\sin\theta$, will result in $T^{-1}_{dipolar}(\mathbf{g}^{f}) < T^{-1}_{dipolar}(g_{average})$, see Figure 8. In this case the approximative values of $T^{-1}_{dipolar}(g_{average})$ are *higher* than the real $T^{-1}_{dipolar}(\mathbf{g}_{f})$ values. This means, that for $g^{f}_{i} < g^{s}$ in cases of distance estimate from $T^{-1}_{dipolar}$ the calculated distance will be *underestimated* if one uses the $g_{average}$ instead of $\mathbf{g}_{f}$.

(e) The influence of T_{1fast}, $T_{2\ fast}$: The role of the T_{1fast} and $T_{2\ fast}$ influences the relative importance of the spectral density functions $J(\omega_{f} \pm \omega_{s})$ and $J(\omega_{s})$ which in turn will determine the dipolar relaxation $1/T_{1dipolar}$. A characteristic limit for very fast relaxing metal spin is the case where the value T_{2}^{f} is determined or "driven by" T_{1}^{f}. In this limit $T_{2}^{f} = T_{1}^{f}$ [2, 9, 12]. Representative cases for $T_{2}^{f} = T_{1}^{f}$ are highlighted in the following. In Figure 9 for an axial g^{f}-tensor and $\beta = 0^{0}$, we observe that the value of $T_{2}^{f} = T_{1}^{f}$ has a strong influence on the $1/T_{1dipolar}$ which depends on θ. For θ values lower than $\sim 54^{0}$ i.e. where the dipolar contribution is minimized, the $1/T_{1dipolar}$ is decreasing for shorter $T_{2}^{f} = T_{1}^{f}$ values approaching the limit where $w_{s}T_{1}^{f} \sim 1$ i.e. $T^{1}_{f} \sim 0.017$nsec in the present calculations. On the other hand, for θ values $> 54^{0}$ the $1/T_{1dipolar}$ is enhanced for shorter $T_{2}^{f} = T_{1}^{f}$ values. Shortening of the $T_{2}^{f} = T_{1}^{f}$ values appears to suppress the angular dependent terms, thus the $1/T_{1dipolar}$ profile for the anisotropic g^{f}-tenor resembles that for $g^{f}_{average}$, i..e. see dotted lines in Figure 9.

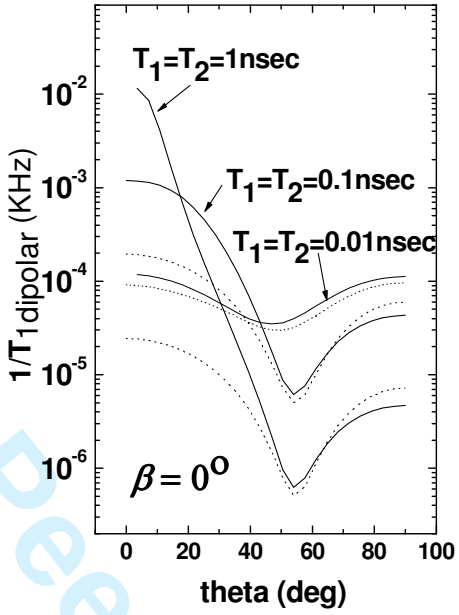

FIGURE 9. Comparison of the effect of the T_1fast and T_2fast on the $1/T_{1dipolar}$ or T_{1fast}=T_{2fast}=1nsec, 0.1nsec, and 0.01nsec respectively. Calculation parameters g^f = [3.0, 3.0, 2.0], β=0^0, , v_{slow} =9.4 GHz, interspin distance R=10Å. In each case the dashed line is the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}$= [g^f_1+g^f_2+g^f_3]/3=2.67.

In Figure 10 for an axial g^f-tensor and β=30^0, the angular dependence becomes more complicated, however that same trends are observed. For all the phi-angles, for θ values lower than ~54^0 , the $1/T_{1dipolar}$ is decreasing for shorter T_2^f =T_1^f values approaching the limit where $w_s T_1^f$ ~ 1 i.e. T^1_f ~ 0.017nsec in the present calculations. In Figure 10, for θ values >54^0 the $1/T_{1dipolar}$ is enhanced for shorter T_2^f =T_1^f values.

Calculations at other beta values, can be easily performed by using expression (25), showing that shortening of the T_2^f =T_1^f values appears to suppress the angular dependent terms, thus the $1/T_{1dipolar}$ profile for the anisotropic g^f-tenor resembles that for $g^f_{average}$,

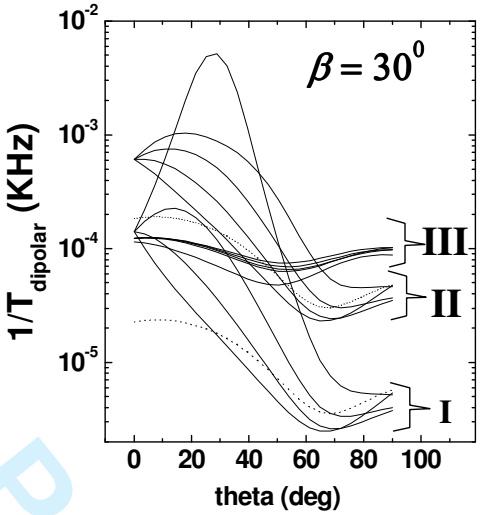

FIGURE 10. Comparison of the effect of the T_1fast and T_2fast on the $1/T_{1dipolar}$. Calculation parameters (**I**) T_1fast=T_2fast=1nsec (**II**) T_1fast=T_2fast=0.1nsec, (**III**) T_1fast=T_2fast=0.01nsec. In all cases $\beta=30^0$, other parameters as in Figure 2. For each case, the dashed lines are the $1/T_{1dipolar}$ calculated by using an isotropic $g_{average}= [g^f_1+g^f_2+g^f_3]/3=2.67$.

Analysis of the spectral density functions $J(w_s)$, $J(w_f \pm w_s)$ provides further useful insight on the relative importance of the various terms. In Figure 11 we present $J(w_s)$, $J(w_f \pm w_s)$ calculated for the case corresponding to the parameters of Figure 9. We notice that at relatively long $T_2^f = T_1^f$ =1nsec, i.e. $w_s T_1^f >> 1$, the spectral density function $J(w_f - w_s)$ is the dominant term, which imposes a strong angular dependence, see Figure 11. This is also the case discussed in Figures 2-8 for even shorter and dissimilar T_2^f and T_1^f. For $T_2^f = T_1^f$ approaching the limit where $w_s T_1^f \sim 1$ i.e. $T^1_f \sim 0.017$nsec, terms $J(w_s)$ become comparable with $J(w_f - w_s)$.

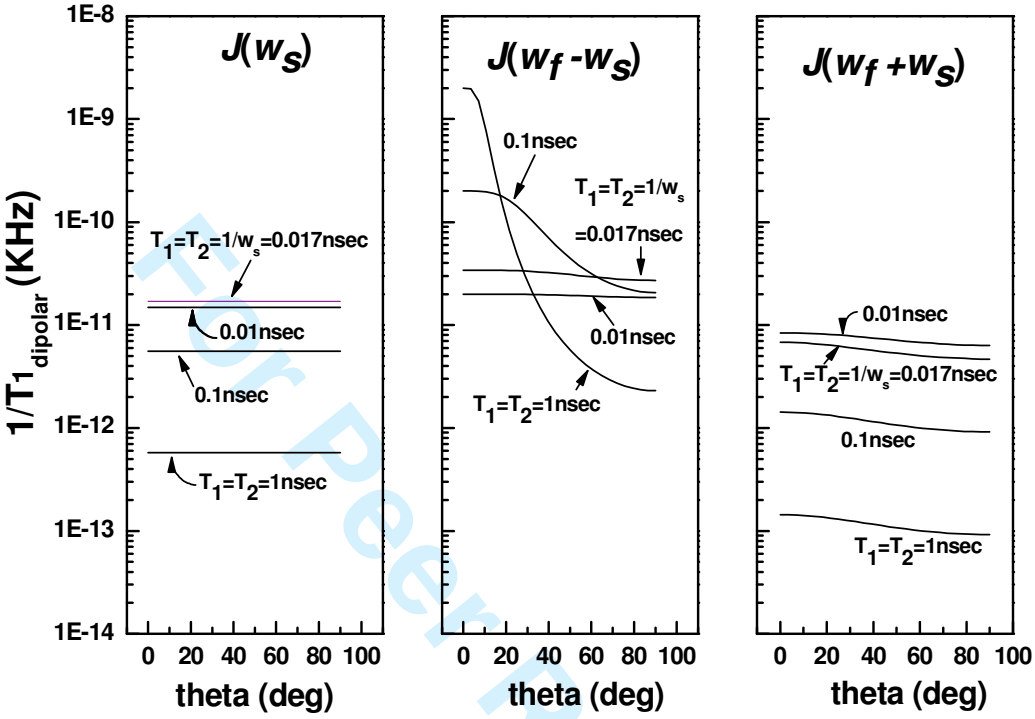

FIGURE 11. Comparison of the effect of the T_1fast and T_2fast on the spectral density functions $J(w_s)$, $J(w_f \pm w_s)$. Other parameters as in Figure 9.

The term $J(w_s)$ is angular independent, therefore its increasing contribution is responsible for the observed smoothing of the angular dependence observed in Figures 9, and similarly in Figure 10, for $T_2^f = T_1^f$ approaching the limit $w_s T_1^f \sim 1$. For $T_2^f = T_1^f$ shorter than $1/w_s$ i.e. see curves for $T_2^f = T_1^f$ = 0.01nsec in Figure 11, all the spectral densities decrease, due to the decoupling of the fast relaxing spin from the slow relaxer.

Overall the discussion at the limit of fast $T_2^f = T_1^f$ reveals that for $T_2^f = T_1^f$ approaching the limit $w_s T_1^f \sim 1$ the term $J(w_s)$ which is angular independent, attains increasing contribution resulting in a smoothing of the angular dependence of the $1/T_{1\text{dipolar}}$.

(f) Powder Saturation Recovery Calculations: Usually the majority of relaxation measurement experiments are carried out in frozen solution or powder samples. A powder saturation recovery curve can be calculated by using equation (25) by summing over a grid of spatial orientations of the magnetic field relative to the interspin vector i.e. over a grid of angles θ and φ. According to standard notation we assume exponential recovery (*2*) with an angular weight function $\sin\theta$ (*2, 12, 20, 24*). Representative powder saturation recovery curves calculated in this way

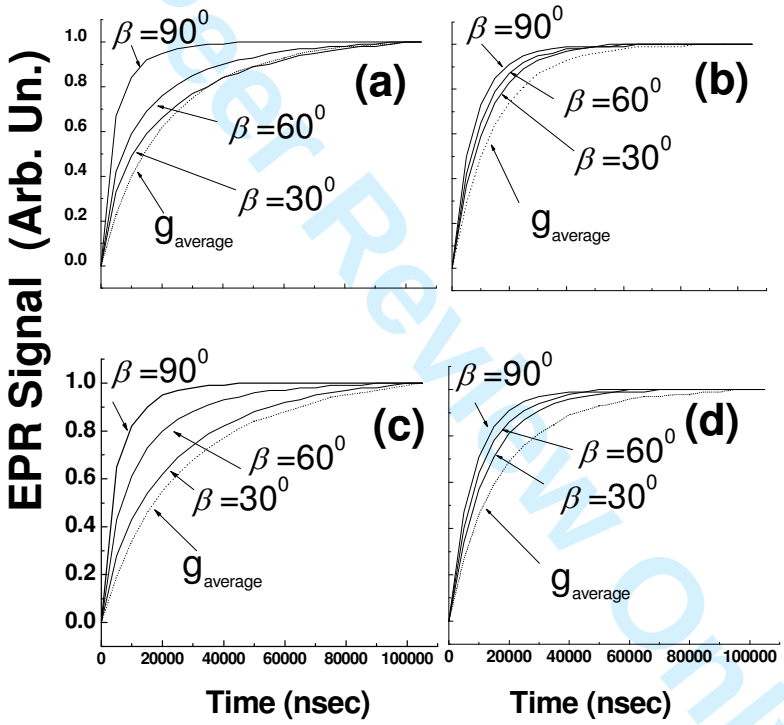

FIGURE 12. Theoretical saturation recovery curves. Calculation parameters (a) Rhombic g^f-tensor: g^f = [3.5, 2.5, 2.0], T_{1fast}=T_{2fast}=0.1nsec. (b) as in (a) with T_{1fast}=, T_{2fast}= 0.01nsec. (c) Axial g^f-tensor:g^f = [3.0, 3.0, 2.0], T_{1fast}=T_{2fast}=0.1nsec (d) as in (c) with T_{1fast}=T_{2fast}=0.01nsec. In all cases g^s =2, v_{slow} = 9.40GHz, interspin distance R=10Å. The dashed lines are calculated by using an isotropic $g_{average}$= [g^f_1+g^f_2+g^f_3]/3.

are displayed in Figure 12. For clarity in order to show up the effect of the dipolar interaction, the intrinsinc relaxation recovery i.e. the exponential due to $1/T_1^{slow}$, has not been included in the curves shown in Figure 12. Panels (a) and (b) concern rhombic g^f-tensor, while panels (c) and (d) concern an axial g^f-tensor. By comparing the powder saturation recovery for the anisotropic g^f-tensors with that calculated by using an isotropic $g_{average}$ we observe that for beta values larger than zero the saturation recovery in the powder spectrum can be sensitive to the details of the orientation of the fast relaxing spin. In all cases we observe a fester recovery for β values approaching 90^0 . This is due to the choice of g_3^f value of 2.0. At $\beta \rightarrow 90^0$ the spectral density $J(w_f - w_s)$ is maximized since the $w_f - w_s$ difference is diminished. With regard to the effect of the T_1^f and T_2^f we observe that for values approaching the limit of 1/ws, i.e. 0.017nsec in the present calculations, the powder saturation recovery becomes less sensitive to the β value. This stems from the smoothening of the angular dependence of the spectral density $J(w_f - w_s)$ and the contribution of the terms J(ws), see Figures 9 and 10.

4. Conclusions

An analytical expression for $1/T_{1dipolar}$, equation (25) has been derived for the general case of a rhombic $\mathbf{g}^f$-tensor. Based on this, the present analysis shows that the orientation of the $\mathbf{g}_f$ plays a significant role. The use of a $g_{average}$ should be treated with caution. On the other hand, however, in any particular experiment where the g^f-orientation is not known, one may perform a grid of estimates based on the particular T_{1f}, T_{2f} and the g_f-values by using the expression (25). This will provide quantitative estimates of the interspin distance limits. Based on this analysis a practical protocol is suggested :

(a) if $g^f_i > g_s$ (no g^f_i is lower than g_s) then the use of $g_{average}$ might give *underestimated* $T^{-1}_{dipolar}$ i.e. *overestimated* interspin distance.

(b) if $g^f_i < gs$ i.e. if some g^f_i is smaller than g_s then the use of $g_{average}$ might give overestimated $T^{-1}_{dipolar}$ i.e. *underestimated* interspin distance.

(c) in any particular experiment where the g^f-orientation is not known, one must perform a grid of estimates based on the particular T_{1f}, T_{2f} and the $\mathbf{g}^f$-values by using the expression (25). This would provide limits for the distance estimation based on the dipolar relaxation enhancement.

Finally in another context, he effects of the $\mathbf{g}^f$-anisotropy, as highlighted here, are expected to be of particular importance in high-field EPR experiments where orientation selection is enhanced.

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