Magnetization dynamics of the material with spin triplet states under the action of a weak varying field and spin-lattice interaction in zero constant field

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Abstract. The anisotropic dynamics of spin triplet states (STS) of molecular single crystals in zero constant and weak varying magnetic fields (weakness means the absence of saturation at the steady state and of the nutation at the pulse EPR) directed along the molecular axes, is analytically investigated. The equations are derived for the free motion of the sample magnetization, describing its linear oscillations along that molecular axis, along which its nonzero initial value was created. The tensor of the steady-state dynamical susceptibility to the varying field is found. The result of the action of a short MW pulse on STS is analytically described, containing a periodic dependence on the pulse duration and its detuning. Abovementioned results can be applied also to I=1 NMR, what is important for nitrogen-containing explosives and narcotics monitoring.

1. Introduction

A spin triplet state (STS) is a quantum state of a system with a spin of quantum number \( S=1 \). The photoexcited (PE) linear polyacene molecules in mixed organic crystals, triplet excitons, \( \text{Cu}^{2+} \) dimers in metal-oxide complexes, and nitrogen nuclei possess such states. PE amino acids in different proteins and other bio-objects possess STS, too. All these materials play important role in science and technique [1]. Organic crystals with STS are used in optoelectronics and in electromagnetic devices, such as flexible OLED (organic light-emitting diodes), solar cells, and masers. Low cost and simple manufacturing are their advantages. It is worth noting that STS of PE pentacene in mixed molecular crystals can be successfully applied for the investigation at room temperature of such new conceptions, as quantum oscillations of nuclear spins and spin entanglement, the latter being important for quantum algorithms. It is self-evident that the success of abovementioned applications is based on the deep insight into the physics of STS.

EPR is a powerful tool for the investigation of the dynamics of STS. At that, it is a well-known method of the nondestructive testing of materials. A great number of EPR experiments on STS with the zero field splitting (ZFS) of their levels were made in zero constant field [1-5]. Zero field (ZF) EPR
allows studying paramagnetic properties and molecular motion with ultrahigh precision under the action of small perturbations, such as the effect of temperature and pressure [1]. The sensitivity of ZF spectroscopy to small shifts in local magnetic fields enables the studies of the effects of the guest-host interactions in diluted organic paramagnets over a wide temperature range [3, 4]. The modest size of the spectrometer without a large magnet, creating constant field, is a significant preference of ZF EPR [1].

As in the usual EPR, so in ZF EPR the observation of the STS response to their excitement by MW field takes place. This response can be free (after the MW cutout) and steady state; besides, the investigation of the spin-lattice relaxation (SLR) – of the process, resulting from the spin interaction with the lattice, is possible with the help of this response. As soon as this response is the reflection of the motion of the full magnetization of the sample, the importance of the obtaining of the equations describing the motion of the components of this magnetization is obvious. The obtaining of such equations at the weak MW field directed along the molecular axes $X,Y,Z$ is one of the tasks of the given paper. The "weakness" of the varying field means that here we use the linearized equations for the sample magnetization, i.e. we exclude from the consideration the saturation of the transitions of the ZFS at the steady state and the magnetization nutation at the pulse EPR.

In addition, the investigation of the spin-lattice relaxation anisotropy on the separate transitions of ZFS in the case of the one-phonon mechanism of relaxation, dominating in experiments of [5], is the purpose of this work. At that, our aim was to check the validity of the supposition of the authors of [5] about the fractal dimensionality of ribonuclease: i.e., to calculate the probabilities of the relaxational transitions between the levels of ZFS of the buried tryptophan residue of ribonuclease (RNase) $T_1$ and to compare the results with the experimental data of [5].

2. Results and discussion

The following exact equations of the free motion of the magnetization $\vec{M}(M_X, M_Y, M_Z)$ of a sample with STS in zero constant field were obtained:

$$\dot{M}_x + (Y - Z)h^{-2}M_x = 0$$

$$\dot{M}_y + (X - Z)h^{-2}M_y = 0$$

$$\dot{M}_z + (X - Y)h^{-2}M_z = 0$$

where $X = D/3 - E$; $Y = D/3 + E$; $Z = -(2/3)D$ are the energies of the STS levels; $D, E$ are the parameters of ZFS, the latter hereafter in this paper is supposed to be well resolved. It should be noted that, as is was expected, these equations does not follow from the corresponding equations for the motion of the magnetization components in the sufficiently strong magnetic field, obtained in [6], at the vanishing value of this field.

The following anisotropic character of STS free motion is seen from equations (1): each component of the sample magnetization $M_X, M_Y, M_Z$ under the conditions of creating its non-zero initial value, accomplishes the linear oscillation along the corresponding axis. This conclusion coincides with the text of § 5 of the Chapter 3 of Abragam, Bleany monograph [7]. These oscillations have frequencies $\omega_0^X \equiv (Y - Z)/\hbar = (D + E)/\hbar$; $\omega_0^Y \equiv (X - Z)/\hbar = (D - E)/\hbar$; $\omega_0^Z \equiv (X - Y)/\hbar = -2E/\hbar$, which, in accord with our supposition, are not coinciding with each other.

The evolution of the magnetization of a sample with STS in a zero constant field under the action of a weak MW field, directed along $X, Y, Z$ axes, correspondingly, is described by the following approximate equations, derived by us:

$$\dot{M}_x + \frac{2\dot{M}_x}{T_2 X} + \frac{(D + E)^2}{h^2}M_x = \frac{8\mu_0D}{h}M_x \frac{D + E}{h} \cdot \frac{\vec{M}_Z}{\hbar} \cdot \vec{M}_x |_{t = t_0} 4B_1 \cos \omega$$

$$\vec{M} = (M_X, 0, 0)$$
\[
\begin{align*}
\ddot{M}_Y &= \frac{2M_Y}{T_{2Y}} + \frac{(D-E)^2}{\hbar^2} M_Y = \frac{g_Y \mu_B}{\hbar} D - E \ddot{M}_Y \mid_{exc} 4B_1 \cos \omega t ; \quad \dot{M} = (0, M_Y, 0) \\
\ddot{M}_Z &= \frac{2M_Z}{T_{2Z}} + \frac{(2E)^2}{\hbar^2} M_Z = \frac{g_Z \mu_B}{\hbar} 2E \ddot{M}_Z \mid_{exc} 4B_1 \cos \omega t ; \quad \dot{M} = (0, 0, M_Z)
\end{align*}
\]

Here, \(2B_1 \cos \omega t\) is the value of the linear polarized MW field; \(g_{\alpha}\) are the diagonal components of the \(g\)-factor tensor of STS; \(\mu_B\) is the Bohr magneton; the magnetization value \(M^X,Y,Z \mid_{exc}\) characterizes the spin polarization of STS, reached as a result of the photo-exciting. It is seen from these equations that the forced oscillations of the \(\alpha\)-component \(M_{\alpha}\) of the full sample magnetization are induced by the MW field, polarized along the \(\alpha\) axis.

The decay rates \((T_{2X,Y,Z})^{-1}\) of the magnetization components \(M_X, M_Y, M_Z\) to their zero equilibrium values are introduced by us phenomenologically. At the given stage, only one paper [8] is known to us, for which the solutions of these equations are directly applicable at the MW frequency sweep. In the sample of this paper (PE naphthalene in diphenyl), the anisotropic broadening of the steady state EPR lines is conditioned by the unresolved hyperfine interaction (HFI) of STS with the protons of their own molecules. Following [9], we describe the decay, caused by the spin distribution over frequencies due to this HFI and other less important broadening causes, by the values \((T_{2X,Y,Z})^{-1}\).

The magnetizations \(M^X,Y,Z \mid_{exc}\) in the r.h.s. of our equations are approximately replaced by their steady values under the conditions of the photo exciting and at the absence of MW field. The fact that the MW field with the frequency about the frequencies of ZFS is not resonant for these components and, therefore, cannot swing their oscillations, is the justification for such replacement. Besides, MW field is weak according to our supposition and cannot cause the saturation of the steady state EPR.

The solving of the (2-4) equations enables us to write the complex tensor of the steady state dynamic susceptibility to the MW field with the frequency \(\omega\), directed along one of the axes \(\alpha = X, Y, Z\):

\[
\chi_{\alpha\beta} = \begin{pmatrix}
X_{XX} & 0 & 0 \\
0 & X_{YY} & 0 \\
0 & 0 & X_{ZZ}
\end{pmatrix},
\]

where

\[
\begin{align*}
\chi_{\alpha\alpha} &= \chi'_{\alpha\alpha} - i \chi''_{\alpha\alpha} = \frac{g_{\alpha} \mu_B \mu_0}{\hbar} \dot{M}_{\alpha} \mid_{exc} \left[ \frac{\omega_{\alpha} - \omega - i \left( T_{2\alpha} \right)^{-1}}{\left( \omega_{\alpha} - \omega \right)^2 + \left( T_{2\alpha} \right)^{-2}} \right],
\end{align*}
\]

\(\omega_{\alpha}\) are the center frequencies of the ZFS transitions, shifted by HFI in the situation of [8].

However, the pulse ZF EPR is of the main interest and actuality [1-4]. Here, we would like to consider the result of the action on STS of the short pulse (with the duration \(\tau_p\), much less than the time of SLR and the reverse line widths of the transitions) of the MW field. The following values of the magnetization \(M^X,Y,Z \mid_{exc} (\tau_p)\), created by the exciting pulse of the MW field along the axis \(X, Y, Z\) can readily be obtained from the Eqs. (2-4) with the help of the corresponding formula from [10]:

\[
M^X,Y,Z \mid_{exc} (\tau_p) = \dot{M}^X,Y,Z \mid_{exc} = \frac{g_{X,Y,Z} \mu_B \mu_0}{\hbar} M^X,Y,Z \mid_{exc} \left[ \frac{\sin \left[ \left( \omega_{\alpha}^X,Y,Z \mid_{exc} - \omega \right) \tau_p / 2 \right]}{\left( \omega_{\alpha}^X,Y,Z \mid_{exc} - \omega \right) \tau_p / 2} \right] \sin \omega_{\alpha}^X,Y,Z \mid_{exc} \tau_p.
\]
Comparing (7) with the formula (7) of [2], it is necessary to note that, as the latter formula, (7) contains the value $\tilde{M}_{X,Y,Z}^{x,y,z}$, reflecting the spin polarization, achieved at the action of the light pulse, preceding the MW pulse. Eq. (7) contains also the double angle $2\theta_p = g_{x,y,z} \mu_B \hbar^{-1} \cdot 2B_{o}^{x,y,z} \tau_p$ of the sample magnetization rotation by the MW pulse of the amplitude $2B_{o}^{x,y,z}$ and the duration $\tau_p$. However, in (7) this angle stands instead of the usual at the nutation of STS $\sin(2\theta_p)$ – see (7) from [2]. This is a consequence of the linearization of our equations, suggesting the fulfillment of the inequality $2\theta_p \ll 1$. From the other hand, our approach allows taking into account the presence of the detuning $(\alpha_{0}^{x,y,z} - \omega)$ of the frequency of the exciting pulse relatively to the ZFS frequencies, which was absent in the equations (7) of [2]. The periodic dependencies of $M_{X,Y,Z}^{x,y,z}(\tau_p)$ envelope value as on the detuning, so on the exciting pulse duration are the interesting results of this accounting. At that, these dependencies have the different form for the different transitions.

The calculation of the probabilities $W_{\xi,\zeta}$ of the one-phonon SLR on the separate STS transitions is performed further. It should be noted that in the experiment of [5] these probabilities at $T_L > 1.2K$ (where the high-temperature approximation (HTA) over the phonon temperature is already valid) increases less rapidly with the level $\xi, \zeta$ splitting than $(\xi - \zeta)^2$, implying that the phonon density of states increases more slowly than usual dependence $(\xi - \zeta)^2$. This supposition agrees with the fractal theory of [11], according to which this density is proportional to $(\xi - \zeta)^{d-1}$, where $d$ is the fractal dimensionality of the "lattice" of a protein type organic crystal. Accounting for this fact, we have obtained the following formula for the probability of the relaxational transitions:

$$W_{\xi,\zeta} = \frac{d \hbar^{-d-1}}{k_B T_L} \frac{2 \pi^2 n^d \nu^d}{6 \pi^2 n^2} \left(\xi - \zeta\right)^d \exp\left[\frac{(\xi - \zeta)/k_B T_L}{\exp[(\xi - \zeta)/k_B T_L]}\right] \sum_{\alpha, \beta} L_{\alpha \beta} \left(\frac{G_{\alpha \beta}^{\zeta}}{G_{\alpha \beta}}\right)^2,$$

where $\xi, \zeta, \zeta$ take the values $X, Y, Z$ and all their cyclic rearrangements; $L_{\alpha \beta} = \frac{k_B T_L}{644 \pi^2 \rho_c}$, $\rho_c$ is the crystal density; $n$ and all their cyclic rearrangements; $\nu$ is the frequency and the velocity of a phonon of the $\nu$ - th branch with the wave vector $k_p$; $\lambda_{\alpha \zeta}$ are the direction cosines of the polarization vector of phonons; $\mu_B$ are the components of the unit wave vector; the integration occurs over the body angle $\Omega$. Taking into account the experimental data for the buried tryptophan residue in RNase T1 in 40% glycerol-phosphate buffer mixture from [5], and also the value of the fractal dimensionality $d = 4/3$ for RNase [12], the temperature dependencies of the probabilities of the separate relaxational transitions were built by us, which agreed well with the experimental points. Due to the accounting for $d = 4/3$, the correlation $W_{\zeta} / W_{\xi} \approx 1.7$, observed in the experiment, takes place with a good accuracy over the temperature range investigated.

3. Conclusion

Summarizing, the following results on the anisotropic spin dynamics of STS of a single crystal in a zero constant magnetic field and a weak varying field, directed along the molecular axes $X, Y, Z$ are obtained:

The equations of the free m...
The tensor of the steady state dynamic susceptibility to a varying field is found; 
At the absence of nutation, the result of the action of the short pulse of a varying field is found to have a periodic dependence on the pulse duration and on the detuning of the pulse frequency relatively to the transition frequency; 
The abovementioned results can be applied also to I=1 NMR, what is important for nitrogen-containing explosives and narcotics monitoring.

The anisotropic dynamics of SLR of the electron STS at the one-phonon mechanism of SLR is investigated without HTA over the phonon temperature: 
The expressions for the SLR probabilities of separate ZFS transitions are found to be proportional to the $d$ power of the splitting of the corresponding transitions at temperatures close to 0° K. The successful comparison is carried out with the corresponding results of [5] for the buried residue of tryptophan of ribonuclease $T_1$ at low temperatures. At that, the supposition of the authors of [5] about the fractal dimensionality $d$ of RNase $T_1$ is verified.

References

[1] Lin T-S 2018 *J. Chin. Chem. Soc.* **65** 163
[2] Yang T-C, Sloop D, Weissman S and Lin T-S 2000 *J. Chem. Phys.* **113** 11194
[3] Lang J, Sloop D and Lin T-S 2007 *J. Chem. Phys.* **111** 4731
[4] Lin T-S, Yang T-C and Sloop D 2013 *Chemical Physics* **422** 251
[5] Ghosh S, Petrin M and Maki A 1986 *Biophys. J.* **49** 753
[6] Fokina N, Khalvashi E and Elizbarashvili M 2019 *Anisotropic Evolution of the Spin-Triplet States Under the Action of the Varying Fields and the Lattice in a Nonzero Constant Field* Available at: https://doi.org/10.1007/s10948-019-5014-7
[7] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon Press)
[8] Clyde A, Hutchison Jr, Nicholas J and Scott G 1970 *J. Chem. Phys.* **53** 163
[9] Salikhov K, Semenov A and Tsvetkov Yu 1976 *Electron Spin Echo and its Applications* (Novosibirsk: Nauka) pp 15–6
[10] Rabinovich M and Trubetskoy D 1989 *Oscillations and Waves: in Linear and Nonlinear Systems* (Dordrecht; Boston; London: Kluwer Academic Publishers) p 13
[11] Allen J, Colvin J, Stinson D, Flynn C and Stapleton H 1982 *Biophys. J.* **38** 229
[12] Torrens F 2001 *Complexity International* **08** 1