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Investigation of Spin-Lattice Relaxation in the Excited Triplet States of Impure Molecular Crystals Induced by the Translational and Rotational Motions of the Molecule

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The direct one-phonon processes of spin-lattice relaxation (SLR) in the excited triplet states of organic molecular crystals are investigated at low temperatures and high magnetic fields. The mixing of the translational and rotational motions of the molecule (TRM relaxation mechanism) is chosen as the major mechanism, leading to the coupling of the spin system with acoustic vibrations. The angular, field and temperature dependences of SLR rate are calculated for an isotopic impurity in deuterobenzophenone crystal using the atom-atom potentials method of the intermolecular interaction. The anisotropy of the electronic $\hat{g}$-tensor is analyzed. The obtained results are in accordance with available experimental data.

Keywords: Spin-lattice relaxation; isotopic impurity; lattice dynamics; atom-atom potentials

INTRODUCTION

The relaxation processes between the spin sublevels of excited triplet states in molecular crystals are investigated to obtain information about the excited states. Because of the strong anisotropy of the intermolecular interactions in organic molecular crystals the translational motions are accompanied by a simultaneous rotation of the molecules, i.e. mixing of the translational and rotational motions takes place. The TRM mechanism allows the anisotropic interaction energy of the fine-structure (FS) of spin sublevels and the

anisotropic $\hat{g}$-tensor of the spectroscopic splitting to be modulated by the acoustic phonons and is the main source of low-temperature SLR in organic crystals [1–5].

In the present paper within the framework of the TRM mechanism the direct one-phonon SLR processes were studied in details. The investigation of the field, angular and temperature dependencies of SLR rates for the real model of deuterobenzophenone crystal with isotopic impurity has been carried out using the atom-atom potentials method [6–7]. The obtained numerical values of SLR time and the dependence of SLR probability on the magnetic field strength are in accordance with available experimental data [8–9].

CALCULATION OF SLR PROBABILITIES IN THE TRM MECHANISM

Consider the triplet excited impure molecule in organic molecular crystal. The crystal is located in a magnetic field with strength $\vec{B}$. Assume that the spin energy in the magnetic field exceeds considerably the FS energy, so spin sublevels can be classified by spin projection on the magnetic field σ. Let us investigate the probabilities of SLR transitions between the triplet sublevels of the impure molecule. According to the results [4–5] the spin-phonon interaction Hamiltonian is given by

$$H_{\text{TRM}} = \sum_{\mu} \left[\frac{\partial H_Z}{\partial \Theta_\mu} + \frac{\partial H_{\text{FS}}}{\partial \Theta_\mu} \right] \Theta_\mu^{(t)}, \tag{1}$$

where H_Z is the operator of Zeeman interaction and H_{FS} is the electron spin-Hamiltonian in zero field, which gives rise to the FS of the EPR spectrum.

$\Theta_\mu^{(t)}$ is an infinitesimal rotation angle about the μth molecular axis:

$$\Theta_\mu^{(t)} = \sum_{\vec{f}_j} \left[\frac{\hbar}{2NI_\mu \omega_{\vec{f}j}} \right]^{1/2} e_\mu(\vec{f}\,j) \left[q_{\vec{f}_j}^{+} \exp(i\omega_{\vec{f}_j} t) + \text{h.c.} \right] \tag{2}$$

Here N is the number of the unit cells of the crystal; I_μ is the μth component of the moment of inertia of the molecule; $\vec{f}$ is the phonon wave vector; $e_\mu(\vec{f}\,j)$ is the μth component of the polarization vector; $q_{\vec{f}_j}^{+}$ is the phonon birth operator of the jth acoustic branch; $\omega_{\vec{f}_j}$ is the vibration frequency,

determined by the dispersion law

$$\omega_{\vec{f}j} = \left[\sum_{\mu} f_{\mu}^2 v_{\mu,\vec{f}j}^2\right]^{1/2}, \tag{3}$$

in which $v_{\mu,\vec{f}j}$ is the μth component of the phase velocity.

We choose the coordinate system with $Z \| \vec{B}$. The Hamiltonian (1) can be rewritten as

$$H_{\text{TRM}} = \sum_{L=1}^{2} \sum_{M=-L}^{L} \sum_{\mu} T_M^L P_{\mu}^{LM} \Theta_{\mu}^{(t)}, \tag{4}$$

where T_M^L is an irreducible tensor operator [10] and P_{μ}^{LM} are the constants whose non-zero values are the linear combinations of FS parameters D and E and the quantities $\delta g_{\mu\mu}$ which describe the anisotropy of $\hat{g}$-tensor [11]:

$$P_X^{10} = (2)^{1/2}\beta(\delta g_{ZZ} - \delta g_{YY})B_Y$$

$$P_Y^{10} = (2)^{1/2}\beta(\delta g_{XX} - \delta g_{ZZ})B_X$$

$$P_X^{1\mp 1} = i\beta(\delta g_{ZZ} - \delta g_{YY})B_Z$$

$$P_Y^{1\mp 1} = \pm\beta(\delta g_{XX} - \delta g_{ZZ})B_Z$$

$$P_Z^{1\mp 1} = \beta(\delta g_{YY} - \delta g_{XX})\ (iB_X \pm B_Y)$$

$$P_X^{2\mp 1} = i(D+E);\ P_Y^{2\mp 1} = \mp(D-E);\quad P_Z^{2\mp 2} = \mp i2E \tag{5}$$

Regarding the operator (4) to be a perturbation we calculate the transition probability between spin sublevels of the impurity with projections of magnetic moments σ and σ' ($\sigma, \sigma' = 0, \mp 1$)

$$W_{\sigma\sigma'} = \frac{1}{\hbar^2} \sum_{\mu,\nu} I_{\mu\nu}(\omega_{\sigma\sigma'}) A_{\mu}^{\sigma-\sigma'} \bar{A}_{\nu}^{\sigma-\sigma'}, \tag{6}$$

where

$$A_{\mu}^{\sigma-\sigma'} = \sum_{L,M} \left(\frac{2L+1}{3}\right)^{1/2} C_{1\sigma' L\,\sigma-\sigma'}^{1\sigma} D_{M\sigma-\sigma'}^{L} P_{\mu}^{LM} \tag{7}$$

Here $C^{1\sigma}_{1\sigma' LM'}$ are Klebsh-Gordon coefficients and $D^{L}_{MM'}$ are Wigner functions [10] which describe the orientation of the magnetic field vector $\vec{B}$ with respect to the equilibrium position of the molecular axes. The dependence of relaxation transition rates on temperature and magnetic field is given by the correlation function $I^{(\omega)}_{\mu\nu}$:

$$I^{(\omega)}_{\mu\nu} = \int_{-\infty}^{+\infty} \langle \Theta^{(t)}_{\mu} \Theta^{(0)}_{\nu} \rangle_T \exp(i\omega t)\, dt \tag{8}$$

The averaging in (8) is performed at the equilibrium of the phonon system.

During the SLR rates calculation the main difficulty is the calculation of correlation function (8) from microscopic theory. For the calculation exact data about the constants which characterize the dynamics of real lattice crystal with accounting of impure molecule influence are necessary. However for the isotopic impurity at the frequencies considerably less the limiting frequency of acoustic phonons or for the impurity with insignificant changing of the force constants in comparison with the force constants of the pure crystal during the calculation of $I^{(\omega)}_{\mu\nu}$ we can use the ideal crystal lattice dynamics data [3]. In this case for the correlation function $I^{(\omega)}_{\mu\nu}$ we have

$$I^{(\omega)}_{\mu\nu} = \frac{\hbar V_0}{2\pi} (\omega T^{(0)}_{\mu\nu} + \omega^3 T^{(1)}_{\mu\nu} + \omega^5 T^{(2)}_{\mu\nu}) \left[1 - \exp\left(-\frac{\hbar\omega}{kT} \right) \right]^{-1}, \tag{9}$$

where V_0 is the volume of the unit cell of the crystal and

$$T^{(0)}_{\mu\nu} = (I_\mu I_\nu)^{-1/2} e_\mu(0)\, e_\nu(0) \sum_j \langle v^{-3}_{\vec{n}j} \rangle_{\vec{n}}$$

$$T^{(1)}_{\mu\nu} = -(I_\mu I_\nu)^{-1/2} e_\mu(0) \sum_j \langle e^{(1)}_\nu(\vec{n}j)\, v^{-5}_{\vec{n}j} \rangle_{\vec{n}}$$

$$T^{(2)}_{\mu\nu} = \frac{1}{4} (I_\mu I_\nu)^{-1/2} \sum_j \langle e^{(1)}_\mu(\vec{n}j)\, e^{(1)}_\nu(\vec{n}j)\, v^{-7}_{\vec{n}j} \rangle_{\vec{n}} \tag{10}$$

The averaging in (10) is performed on all possible orientations of vector $\vec{n} = \vec{f}/|\vec{f}|$.

In the present paper the values of $T^{(i)}_{\mu\nu} (i = 0, 1, 2)$ were found from the analysis of the lattice dynamics equations in the longwave limit ($\vec{f} \to 0$), in

which the TRM of motions of the molecules can be accounted for by perturbation theory (Appendix).

For an isotopic impurity in a crystal of deuterobenzophenone the quantities $T_{\mu\nu}^{(i)}$ were calculated numerically using the atom-atom potentials method [8–9] and the data of molecular crystals structure [12–13]. The calculation has shown that the $T_{YY}^{(i)}$ elements dominates: $T_{YY}^{(0)} = T_0 = 1.6 \times 10^{16}$, $s^3/(\mathrm{g} \times \mathrm{cm}^5)$, $T_{YY}^{(1)} = T_1 = 1.1 \times 10^{-6} s^5/(\mathrm{g} \times \mathrm{cm}^5)$, $T_{YY}^{(2)} = T_2 = 1.3 \times 10^{-31} s^7/(\mathrm{g} \times \mathrm{cm}^5)$, where Y is the long axis of the impure molecule. The other elements on two-three orders of the magnitude smaller. Thus, the rotation of the molecule about an axis close to its long axis of inertia takes place.

The results of numerical analysis of the parameters $T_{\mu\nu}^{(i)}$ allow us to simplify the expressions for the SLR probabilities

$$W_{10} = (a_1 B + a_2 \sin\varphi B^2 + (a_3 + a_3' \sin\varphi) B^3 + a_4 \sin\varphi B^4 + (a_5 + a_5' \sin\varphi) B^5) \left[1 - \exp\left(-\frac{g_0 \beta B}{kT}\right)\right]^{-1} \cos^2\varphi$$

$$W_{1-1} = 2(a_1(2B) + a_3(2B)^3 + a_5(2B)^5) \left[1 - \exp\left(-\frac{2g_0 \beta B}{kT}\right)\right]^{-1} \sin^2\varphi, \qquad (11)$$

where the constants of the spin-phonon coupling are defined by:

$$a_1 = \frac{g_0 \beta V_0 T_0 (D-E)^2}{4\pi\hbar^2}$$

$$a_2 = -\frac{g_0 \beta^2 V_0 T_0 (D-E)(\delta g_{XX} - \delta g_{ZZ})}{2\pi\hbar^2}$$

$$a_3 = \frac{(g_0\beta)^3 V_0 T_1 (D-E)^2}{4\pi\hbar^4}$$

$$a_3' = \frac{g_0^2 \beta^3 V_0 T_0 (\delta g_{XX} - \delta g_{ZZ})}{4\pi\hbar^2}$$

$$a_4 = -\frac{g_0^3 \beta^4 V_0 T_1 (D-E)(\delta g_{XX} - \delta g_{ZZ})}{2\pi\hbar^4}$$

$$a_5 = \frac{(g_0\beta)^5 V_0 T_2 (D-E)^2}{4\pi\hbar^6}$$

$$a'_5 = \frac{g_0^4 \beta^5 V_0 T_1 (\delta g_{XX} - \delta g_{ZZ})}{4\pi\hbar^4} \tag{12}$$

Here φ is the angle between the magnetic field vector $\vec{B}$ and the long molecular axis; g_0 is the g-factor of electron.

The calculation values of the relaxation transition probability W_{10} at the different temperatures and magnetic fields and $\varphi = 0$ are given in Table.

TABLE The calculated values of SLR probability W_{10} at the different magnetic fields and temperatures for the direct one-phonon processes

		W_{10}, s^{-1}		
T, K	$B = 1\ T$	$B = 5$	$B = 10$	$B = 20$
1	1.3	7.6×10^1	7.5×10^2	1.08×10^4
4.2	3.8	1.1×10^2	8.2×10^2	1.09×10^4
10	8.4	1.9×10^2	1.2×10^3	1.3×10^4

DISCUSSION

In this paper the SLR rates in the TRM mechanism has been calculated without any fitting parameter in the case of an isotopic impurity. A comparison with the experimental data for a benzophenone molecule in the deuterobenzophenone crystal [6–7] shows that the calculated SLR rate W_{10} for the direct one-phonon processes is of the same order as the experimental ones.

The SLR probabilities W_{10} and W_{1-1} have different angular dependences. Consequently the relaxation processes can be investigated by the selective way. For example, only probability of transition W_{10} is different from zero at the orientation of the magnetic field $\varphi = 0$.

The SLR probabilities W_{10} and W_{1-1} have the different field dependence. It is allows to investigate the relaxation processes in the different regions of the magnetic fields. Because of the small anisotropy of $\hat{g}$-tensor of the spectroscopic splitting, the items, where the a_1, a_3 and a_5 parameters are present, will give the maximum contribution to the SLR. The numerical calculation has shown that the field dependence $W \sim B^3$ takes place in the region of the magnetic field $B < 16\,\mathrm{T}$ and with the increasing of the magnetic field we have $W \sim B^5$. This effect was observed on the experiment [7] in the region of magnetic field strength $B = 20$ T, that confirm about the

relative correction constants of the spin-phonon coupling calculated by us from microtheory.

The expressions for the rates of relaxation transitions depend on the same parameters $T^{(i)}_{\mu\nu}$, defining by the lattice dynamics. The comparison of values $T^{(i)}_{\mu\nu}$, obtained experimentally from the data of measurements W_{10} and W_{1-1} at the different magnetic field orientation would allow to identify the TRM mechanism of spin-phonon interaction. On the other hand, the founded values of $T^{(i)}_{\mu\nu}$ can be used for more precise definition of the lattice structure parameters.

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APPENDIX

The calculation of $e_\mu(\vec{f}\,j)$ within the perturbation theory

Represent the amplitude vector of the displacement molecule of benzophenone crystal (the spatial group $P_{2_12_12_1}, Z=4$) in the form of column vector $\vec{e} = \begin{bmatrix} \vec{e}^{\,t} \\ \vec{e}^{\,r} \end{bmatrix}$, in which the translational ($\vec{e}^{\,t}$) and rotational ($\vec{e}^{\,r}$) components are picked out, and write the equations of lattice motion

$$\hat{T}\vec{e} = \omega^2\vec{e}, \tag{A.1}$$

where $\hat{T}$ is the blocks dynamic matrix which describe the elastic interactions during the translational and rotational molecule motions and the TRM as well.

In the longwave limit ($\vec{f} \to 0$) the dynamic matrix of the crystal is determined:

$$\hat{T}(\vec{f}) = \hat{T}(0) + \delta\hat{T}(\vec{f}) \tag{A.2}$$

The vectors $\vec{e}^{\,t}_0 = \vec{e}^{\,t_0}_{\text{opt},\alpha}, \omega = \omega_{0\,\text{opt},\alpha} \neq 0$ and $\vec{e}^{\,r}_0 = \vec{e}^{\,rc}_{\text{lib},\lambda}, \quad \omega = \omega_{0\,\text{lib},\lambda} \neq 0$, which describe the limiting values of the optical and librational vibrations are calculated using the equation (A.1) at $\vec{f} = 0$. The three vectors $\vec{e}^{\,t}_0 = \vec{e}^{\,\text{to}}_{ak,\alpha}$ corresponding to the triply degenerate eigenvalue $\omega = 0$ can be chosen parallel to the crystal axes.

The TRM of motions implies that the acoustic vibrations have the translational as well as rotational components. Using the limiting values of the vectors and frequencies as a zeroth approximation and taking into account the relations (A.1),(A.2) it is possible to find these components from the perturbation theory at $\vec{f} \to 0$. In the linear dispersion region their translational components do not contain any limiting optical phonons and determined by the equation

$$[\hat{\Lambda}(\vec{n}) - v_j^2(\vec{n})]\ \vec{e}^{\,t}_{ak}(\vec{n}j) = 0, \tag{A.3}$$

in which $v_j(\vec{n})$ is the phase velocity of the jth branch phonon propagating in the direction $\vec{n} = \vec{f}/|\vec{f}|$, defined by the condition that the determinant of equation (A.3) vanish, and

$$\hat{\Lambda}(\vec{n}) = \frac{\partial^2}{\partial f^2}(\delta \hat{T}^{tt}(\vec{f}))_{|\vec{f}\to 0} \tag{A.4}$$

The rotational component of the amplitude vector of this phonon has the form:

$$\vec{e}^{\,r}_{ak}(\vec{n}j) = \vec{e}^{\,r}_{ak}(0) + \sum_{\lambda} \vec{e}^{\,rc}_{\text{lib},\lambda} \frac{(\vec{e}^{\,rc}_{\text{lib},\lambda}, \delta \hat{T}(\vec{f})\, \vec{e}^{\,t}_{ak}(\vec{n}j))}{\omega^2_{0\,\text{lib},\lambda}} \tag{A.5}$$

Introducing the notation $u_{\lambda\mu}$ for the projection of the limiting amplitude vector of the λth librational vibration on to the μth axis of molecule and

$$\delta T^{rt}_{\lambda}(\vec{n}j) = \frac{\partial^2}{\partial f^2}(\vec{e}^{\,rc}_{\text{lib},\lambda}, \delta \hat{T}(\vec{f})\, \vec{e}^{\,t}_{ak}(\vec{n}j))_{|\vec{f}=0} \tag{A.6}$$

we obtain an expression for the amplitude of the rotation molecule around its μth axis under the action of the acoustic vibration

$$e_{\mu}(\vec{f}j) = e_{\mu}(0) - \frac{1}{2} f^2 e^{(1)}_{\mu}(\vec{n}j), \tag{A.7}$$

where

$$e^{(1)}_{\mu}(\vec{n}j) = \sum_{\lambda} u_{\lambda\mu} \delta T^{rt}_{\lambda}(\vec{n}j)\, \omega^{-2}_{0\,\text{lib},\lambda} \tag{A.8}$$

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