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SPIN-LATTICE RELAXATION IN THE PHOTOEXCITED TRIPLET STATE OF SOLID C_{60}: CONSIDERATION OF SPIN-ORBITAL INTERACTION

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The spin-lattice relaxation (SLR) mechanism based on the energy modulation of spin-orbital interaction (SOI) has been investigated in the photoexcited triplet states of a fullerene crystal C_{60}. This modulation emerges as a result of admixture of rotational motions of a molecule and vibrational motions of the nuclei to the translational molecular motions at the acoustic lattice vibrations. Simple expressions for SLR rates of direct one-phonon processes are obtained using the atom-atom potentials and molecular orbitals (MO) methods. The influence of the dynamic Jahn-Teller (JT) effect in a molecule C_{60} on the SLR rates is analyzed. A comparison of the calculated values for SLR time with available experimental data is carried out.

1. Introduction

The discovery of fullerene molecules [1] and a simple method to condense them to a solid phase found by [2] have boosted studies of the physics and chemistry of these interesting molecules. One of the important electronic properties of fullerene molecules concerns the excited triplet state which has been observed in the experiments [3-12] by ODMR, EPR and ESR techniques. The relaxation processes between spin sublevels of excited triplet states in a solid phase of C_{60} are studied to obtain information about the excited state [12].

In the present paper the SLR of the photoexcited triplet states in a fullerene crystal C_{60} is investigated using a spin-phonon interaction mechanism [13-14] which is based on the energy modulation of SOI. In organic molecular crystals the amplitude displacement vector for acoustic phonons consists of the vibrational components and the components describing intramolecular displacements of the nuclei from an equilibrium position. These types of motions cause the rotation of molecules and alter the intramolecular distributions of the electron density. In this case the anisotropic spin-spin interactions are modulated by low-frequency acoustic vibrations and the following channels of SLR in the triplet excited states are realized: the TRM mechanism (the mixing of translational and rotational motions of a molecule) [15-17] and the TVM mechanism (the mixing of translational motions of a molecule and vibrational motions of the nuclei) [18-19]. On the other hand, analysis of the TRM and TVM of motions has shown that these types of motion can modulate SOI too [13-14]. SOI gives a contribution to the zero-field splitting and induces relaxation transitions between spin sublevels of the triplet excited states.

The field, angular and temperature dependencies of SLR rates for direct one-phonon processes have been investigated by the atom-atom potentials [20] and MO [21-22] methods. The influence of the dynamic JT effect in a molecule C_{60} [23] on SLR rates is analyzed. A comparison of the calculation results for SLR time with the available experimental data [12] is carried out.

2. Hamiltonian of the problem

Let us consider the photoexcited triplet state in a fullerene C_{60} 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 SOI energy, so spin sublevels can be classified by a spin projection on the magnetic field σ ($\sigma = 0, \pm 1$). According to the results [13-14] the Hamiltonian of SOI can be presented in the form (we have used the second order perturbation theory)

$$H_{SOI} = \sum_{\mu,\nu} D_{\mu\nu} S_\mu S_\nu, \tag{1}$$

where in the system of principal axes of the photoexcited molecule C_{60} (symmetry group I_h)

$$D_{\mu\mu} = \sum_n \Big[E_n^0 - E_T^0\Big]^{-1} B_\mu^n (B_\mu^n)^*. \tag{2}$$

Here μ denotes the molecular axes X, Y and Z; E_n^0 and E_T^0 are the energies of the singlet and triplet states in the zeroth approximation, respectively;

$$B_\mu^n = \frac{e^2\hbar}{4m^2c^2} \sum_k Z_k^* \langle T| \frac{L_{1k}^\mu}{R_{1k}^3} - \frac{L_{2k}^\mu}{R_{2k}^3} |n\rangle, \tag{3}$$

where Z_k^* is the effective Slater charge of the kth nucleus of a carbon atom; L_{1k}^μ is the μth component of the orbital moment of the first π-electron given in the coordinates of the kth nucleus; R_{1k} is the distance between the first π-electron and the kth nucleus.

Let us analyze the possible SLR channels in the triplet excited states of a fullerene molecule C_{60} proceeding from the Hamiltonian (1).

1. The interaction of the spin system with an acoustic wave takes place due to a variation of $D_{\mu\mu}$ components, caused by the rotations of molecules upon a displacement of their mass centers (mechanism 1). This interaction is described by the Hamiltonian [13-14]

$$\delta H_{SOI}^{(1)} = \sum_\mu \frac{\partial H_{SOI}}{\partial \Theta_\mu} \delta\Theta_\mu(t), \tag{4}$$

where $\delta\Theta_\mu(t)$ is an angle of infinitesimal rotation of the photoexcited molecule around its μth principal axis of inertia:

$$\delta\Theta_\mu(t) = \sum_{\vec{f}j} \Big[\frac{\hbar}{2NI_\mu\omega_{\vec{f}j}}\Big]^{1/2} e_\mu(\vec{f}j) \Big[q_{\vec{f}j}^+ \exp\Big(i\omega_{\vec{f}j}t\Big) + h.c.\Big]. \tag{5}$$

Here N is the number of unit cells in a crystal; I_μ is the μth component of inertia moment; $\vec{f}$ is the phonon wave vector; $e_\mu(\vec{f}j)$ is the μth polarization vector component; $q^{+}_{\vec{f}j}$ is the phonon creation operator of the jth acoustic branch; $\omega_{\vec{f}j}$ is vibration frequency described by the dispersion law

$$\omega_{\vec{f}j} = \Big[\sum_{\mu} f_{\mu}^{2} v_{\mu,\vec{f}j}^{2}\Big]^{1/2}, \tag{6}$$

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

We choose the coordinate system with $Z||\vec{B}$. Then the spin-phonon interaction (4) can be rewritten as [13-14]

$$\delta H^{(1)}_{SOI} = \sum_{\mu,M} T^{2}_{M} P^{M}_{\mu} \delta\Theta_{\mu}(t), \tag{7}$$

where T^{2}_{M} is an irreducible tensor operator [24]; the non-zero values of the constants P^{M}_{μ} are linear combinations of the quantities $D_{\mu\mu}$ (2):

$$\begin{aligned} P^{\pm 1}_{X} &= i\left(D_{ZZ} - D_{YY}\right), \\ P^{\pm 1}_{Y} &= \pm\left(D_{ZZ} - D_{XX}\right), \\ P^{\pm 2}_{Z} &= \pm i\left(D_{XX} - D_{YY}\right). \end{aligned} \tag{8}$$

2. The change of the nuclei configuration of a molecule in the field of an acoustic wave is due to the modulation of SOI which induces the SLR between spin sublevels of the triplet excited state (mechanism 2). According to the results [13-14] the corresponding spin-phonon interaction Hamiltonian is given by

$$\delta H^{(2)}_{SOI} = \sum_{k,\mu} \frac{\partial H_{SOI}}{\partial R_{k\mu}} \delta R_{k\mu}(t), \tag{9}$$

where $\delta R_{k\mu}$ is the μth component of the displacement of the kth nucleus:

$$\delta R_{k,\mu}(t) = \sum_{\vec{f}j} \Big[\frac{\hbar}{2NM\omega_{\vec{f}j}}\Big]^{1/2} e_{k\mu}(\vec{f}j) \Big[q^{+}_{\vec{f}j} \exp\Big(i\omega_{\vec{f}j}t\Big) + h.c.\Big]. \tag{10}$$

Here M is the mass of the carbon atom nucleus; $e_{k\mu}(\vec{f}j)$ is the μth component of the amplitude displacement of the kth nucleus.

In the coordinate system with $Z||\vec{B}$ the Hamiltonian (9) can be rewritten as [13-14]:

$$\delta H^{(2)}_{SOI} = \sum_{k} \sum_{\mu,M} T^{2}_{M} P^{M}_{k\mu} \delta R_{k\mu}(t). \tag{11}$$

The Non-zero values of the quantities $P^{M}_{k\mu}$ are equal to

$$\begin{aligned} P^{0}_{kX} &= -\left(\tfrac{2}{3}\right)^{1/2} D^{k}_{XX}, \\ P^{0}_{kY} &= -\left(\tfrac{2}{3}\right)^{1/2} D^{k}_{YY}, \end{aligned}$$

$$\begin{aligned} P_{kZ}^{0} &= 2\left(\tfrac{2}{3}\right)^{1/2} D_{ZZ}^{k}, \\ P_{kX}^{\pm 2} &= D_{XX}^{k}, \\ P_{kY}^{\pm 2} &= -D_{YY}^{k}, \end{aligned} \tag{12}$$

where

$$D_{\mu\mu}^{k} = \sum_{n} \left[E_n^0 - E_T^0\right]^{-1} \tilde{B}_{\mu}^{n} (\tilde{B}_{\mu}^{n})^{*} \tag{13}$$

and

$$\tilde{B}_{\mu}^{n} = \frac{e^2 \hbar}{2m^2 c^2} Z_k^{*} \langle T| \frac{R_{1k\mu} L_{1k}^{\mu}}{R_{1k}^5} - \frac{R_{2k\mu} L_{2k}^{\mu}}{R_{2k}^5} |n\rangle. \tag{14}$$

Expressions for the calculation of transition probabilities in the approximation of a high magnetic field are presented in Sec.3.

3. Direct one-phonon relaxation processes

1. Regarding the operator (7) as a perturbation we calculate the SLR transitions probability between spin sublevels σ and σ' of the photoexcited molecule (mechanism 1) [13-14]

$$W_{\sigma\sigma'}^{(1)} = \frac{|\sigma - \sigma'|}{2h^2} \sum_{\mu,\nu} I_{\mu\nu}(\omega_{\sigma\sigma'}) A_{\mu}^{\sigma-\sigma'} A_{\nu}^{\sigma-\sigma'}, \tag{15}$$

where

$$A_{\mu}^{\sigma-\sigma'} = \sum_{M} D_{M\,\sigma-\sigma'}^{2} P_{\mu}^{M}. \tag{16}$$

Here $D_{M\,\sigma-\sigma'}^{2}$ are the Wigner functions [24] describing the orientation of the magnetic field vector $\vec{B}$ relative to the equilibrium position of the molecular axes.

Dependence of relaxation transition rates on temperature and magnetic field is given by the correlation function $I_{\mu\nu}(\omega)$:

$$I_{\mu\nu}(\omega) = \int_{-\infty}^{\infty} \langle \delta\Theta_{\mu}(t) \delta\Theta_{\nu}(0) \rangle_T \exp(i\omega t) \mathrm{d}t. \tag{17}$$

Averaging in (17) is performed over the equilibrium distribution of phonons.

The main difficulty in the calculation of the SLR rates from formula (15) is finding the quantities P_{μ}^{M} (8) with the help of quantum-chemical methods (in particular, the Parizer-Parr-Pople (PPP) MO method in combination with the configuration interaction (CI) [21-22]), and also the correlation function (17) from the microscopic theory. For these calculations we need exact data on the constants characterizing the lattice dynamics of a real C_{60} crystal with taking into account the photoexcited molecule influence (the observed EPR spectra indicate that the geometry of the C_{60} molecule is distorted from the soccerball geometry in the excited triplet state [4]).

However, at the frequencies considerably less than the limiting frequency of acoustic phonons the photoexcited molecule effects are insignificant [15] and during the calculation of $I_{\mu\nu}(\omega)$ we can use the lattice dynamics data for an ideal C_{60} crystal [25]. In this approximation for the correlation function (17) we have

$$I_{\mu\nu}(\omega) = \frac{\hbar V_0}{2\pi} T_{\mu\nu}\omega^3\Big[1 - \exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big]^{-1}, \tag{18}$$

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

$$T_{\mu\nu} = (I_\mu I_\nu)^{-1/2}\sum_j \langle e_\mu(\vec{f}j)e_\nu(\vec{f}j)f^{-2}v_{\vec{f}j}^{-5}\rangle_{\vec{f}}. \tag{19}$$

Averaging in (19) is performed over all possible orientations of the wave vector $\vec{f}$. It is noted that the matrix $T_{\mu\nu}$ in the system of principal axes of the molecule C_{60} is a diagonal one.

In the present paper the values of $T_{\mu\mu}$ were found from the analysis of the lattice dynamics equations in the longwave approximation ($\vec{f} \to 0$), when the TRM can be taken into account through the perturbation theory [16-17].

The quantities $T_{\mu\mu}$ were calculated numerically using the atom-atom potential method [20] and the data of solid C_{60} structure at low temperature $T = (4.2 - 5)K$ (symmetry group $Pa3$, $z = 4$, $a_0 = 14.04$ Å [26-27]). It was found that $T_{XX} \approx T_{YY} \approx T_{ZZ} = T_0 = 3.50 \cdot 10^{10} s^5/(kg \cdot m^5)$.

These results allow us to obtain the following approximate expressions for the SLR rates in the case of direct one-phonon processes

$$W_{10}^{(1)} = a\omega^3\Big[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\Big]^{-1}\left[1 + 29.8\cos^2\varphi + 20.7\cos^2 2\varphi\right], \tag{20}$$

$$W_{1-1}^{(1)} = 16a\omega^3\Big[1 - \exp\left(-\frac{2\hbar\omega}{kT}\right)\Big]^{-1}\left[35.9 - 29.8\cos^2\varphi - 5.2\cos^2 2\varphi\right], \tag{21}$$

where

$$a = \frac{V_0 T_0}{4\pi\hbar}\Big(D_{XX} - D_{YY}\Big)^2. \tag{22}$$

Here φ is the angle between the magnetic field vector $\vec{B}$ and the X molecular axis; ω is the Larmor frequency. For the photoexcited molecule in a fullerene C_{60} crystal the constant of the spin-phonon interaction is equal to $a = 0.56 \cdot 10^{-33} s^2$.

2. Considering operator (11) to be a perturbation we calculate the SLR transition probability between spin sublevels σ and σ' of the photoexcited molecule (mechanism 2) [13-14]

$$W_{\sigma\sigma'}^{(2)} = \frac{|\sigma - \sigma'|}{2h^2}\sum_{k,k'}\sum_{\mu,\nu} I_{\mu\nu}^{kk'}(\omega_{\sigma\sigma'})A_{k\mu}^{\sigma-\sigma'}A_{k'\nu}^{\sigma-\sigma'}, \tag{23}$$

where

$$A_{k\mu}^{\sigma-\sigma'} = \sum_M D_{M\,\sigma-\sigma'}^2 P_{k\mu}^M. \tag{24}$$

Dependence of relaxation transition rates on the temperature and magnetic field is given by the correlation function $I^{kk'}_{\mu\nu}(\omega)$:

$$I^{kk'}_{\mu\nu}(\omega) = \int\limits_{-\infty}^{\infty} \langle \delta R_{k\mu}(t)\delta R_{k'\nu}(0)\rangle_T \exp(i\omega t)\mathrm{d}t. \tag{25}$$

The quantities $P^M_{k\mu}$ (12) in formula (24) were calculated by the PPP MO method in combination with CI [21-22]. For the correlation function (25) the following expression has been obtained (in the same approximations which were used by deriving formula (18) for the correlation function (17))

$$I^{kk'}_{\mu\nu}(\omega) = \frac{\hbar V_0}{2\pi} T^{kk'}_{\mu\nu}\,\omega^5 \Big[1 - \exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big]^{-1}, \tag{26}$$

where

$$T^{kk'}_{\mu\nu} = \frac{1}{M}\sum_j \langle e_{k\mu}(\vec{f}j) e_{k'\nu}(\vec{f}j) f^{-4} v^{-7}_{\vec{f}j}\rangle_{\vec{f}}. \tag{27}$$

It is noted that matrix $T^{kk'}_{\mu\nu}$ in the system of principal axes of the molecule C_{60} is a diagonal one.

We shall find the values of $T^{kk'}_{\mu\mu}$ from the analysis of the lattice dynamics equations in the longwave approximation ($\vec{f} \to 0$), when the TVM can be taken into account through the perturbation theory [18-19].

Quantities $T^{kk'}_{\mu\mu}$ were calculated numerically using the atom-atom potentials method [20] and the molecular dynamics data for a fullerene C_{60} [28] and the lattice dynamics and structure data of a solid C_{60} at low temperature [25-27]. It was found that $T^{kk'}_{XX} \approx T^{kk'}_{YY} \approx T^{kk'}_{ZZ} = T^{kk'}_0$.

Taking into consideration the obtained results for the parameters $T^{kk'}_{\mu\mu}$ we can simplify expression (23) for the transition probabilities

$$W^{(2)}_{10} = b\omega^5\Big[1 - \exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big]^{-1} \sin^2 2\varphi, \tag{28}$$

$$W^{(2)}_{1-1} = 16b\omega^5\Big[1 - \exp\Big(-\frac{2\hbar\omega}{kT}\Big)\Big]^{-1} \left[1.6 - 1.4\sin^2\varphi + \sin^4\varphi\right], \tag{29}$$

where

$$b = \frac{V_0}{2\pi\hbar}\sum_{k<k'} T^{kk'}_0 \Big[D^k_{YY}D^{k'}_{YY} + D^k_{ZZ}D^{k'}_{ZZ}\Big]. \tag{30}$$

For the photoexcited molecule in a fullerene C_{60} crystal the constant of the spin-phonon interaction is equal to $b = 0.23 \cdot 10^{-52} s^4$.

The value of SLR time in mechanism 1 ($i = 1$) and mechanism 2 ($i = 2$) can be calculated by the equation:

$$T^i_1 = \Big(W^{(i)}_{10} + 2W^{(i)}_{1-1}\Big)^{-1}. \tag{31}$$

4. Discussion

Let us analyze expressions (20-21) and (28-29) for relaxation transition probabilities obtained by using mechanism 1 and mechanism 2, correspondingly.

SLR rates for the direct one-phonon processes in mechanism 1 and mechanism 2 have different angular dependencies. It allows us to investigate the relaxation processes in a selective way.

SLR rates for the direct one-phonon processes in mechanism 1 and mechanism 2 have the same temperature dependencies and different magnetic field ones. In the limit cases we have: $W^1 \sim T\omega^2$ and $W^2 \sim T\omega^4$ at $\hbar\omega/(kT) \ll 1$ and $W^1 \sim \omega^3$ and $W^2 \sim \omega^5$ at $\hbar\omega/(kT) \gg 1$. Consequently, relaxation processes can be investigated in different regions of the magnetic field.

Numerical values of SLR time in mechanism 1 and mechanism 2 at different temperature and magnetic fields are given in the table for $\varphi = \pi/2$ ($\vec{B}||Z$, the molecular axis Z is orientated along the axis of symmetry C_2 in a fullerene C_{60}). As we can see at low magnetic fields ($B < 1T$) the values of SLR time in mechanism 2 (see 2 in the table) are of the same order as in mechanism 1 (see 1 in the table). But the contribution of mechanism 2 decreases as compared to mechanism 1 with the increase of the magnetic field ($B \geqslant 1T$). The dominant role of mechanism 1 in comparison with mechanism 2 is explained by the strong TRM of motions [16-17,25] and the weak TVM of motions [18-19].

A comparison with the available experimental data for paramagnetic centers in a polycrystalline C_{60} [12] shows that the calculated SLR times are in satisfactory agreement with experimental ones (see the table). It is confirmed by the relative correction constants of the spin-phonon coupling calculated by us without any fitting parameters in the case of the pho-

SLR mechanism	T_1, s		
	$B = 0.3$ T	$B = 1$	$B = 5$
	$T = 4.2$ K		
1	$2.1 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$
2	$0.5 \cdot 10^{-3}$	$3.2 \cdot 10^{-6}$	$2.1 \cdot 10^{-9}$
	$(0.7 \cdot 10^{-3})^*$		
	$T = 10$		
1	$0.9 \cdot 10^{-3}$	$0.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-6}$
2	$2.1 \cdot 10^{-4}$	$1.6 \cdot 10^{-6}$	$1.5 \cdot 10^{-9}$
	$T = 15$		
1	$0.6 \cdot 10^{-3}$	$0.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-6}$
2	$1.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-6}$	$1.2 \cdot 10^{-9}$
	$T = 20$		
1	$0.5 \cdot 10^{-3}$	$0.4 \cdot 10^{-4}$	$1.3 \cdot 10^{-6}$
2	$1.2 \cdot 10^{-4}$	$1.0 \cdot 10^{-6}$	$0.9 \cdot 10^{-9}$
	$(0.5 \cdot 10^{-3})^*$		

Table 1. Calculated values of SLR time for different magnetic fields and temperatures caused by: 1,2 - relaxation mechanism investigated. $)^*$ - the experimental data [12].

toexcited molecule. Thus, the SOI effect consideration is necessary in the investigation of the excited triplet states in fullerene crystals.

It is important to emphasize that the results of the calculation are sensitive to the accuracy of the lattice dynamics computations. For example, a 15-20 per cent error in the sound velocity determination [25] causes a change in the values of $T_{\mu\mu}$ (19) and$T_{\mu\mu}^{kk'}$ (27) and, correspondingly, in the SLR times by twice.

Let us analyze the influence of the dynamic JT effect in a molecule C_{60} on the values of SLR time. The JT distortions of intramolecular vibrational modes for a C_{60}^{-} anion radical are observed in experiment [29]. Changes of the JT active frequencies as regards the neutral molecule C_{60} are 3-19 per cent. As the values of $T_{\mu\mu}^{kk'}$ (27) are proportional to the fourth power of the vibration frequency [18-19], the values of SLR time in mechanism 2 can increase approximately by a factor of (1.1-1.8). Besides, JT distortions take place in the triplet excited state of C_{60} [4-5,7-8,30]. However, the $D_{\mu\mu}$ (2) (mechanism 1) and $D_{\mu\mu}^{k}$ (13) (mechanism 2) parameters changes due to the dynamic JT effect are small and their contribution to the SLR time is less than 7 per cent.

The obtained values of the SLR time carry information on the lattice dynamics. In particular, it concerns the coupling between translations and rotations of the molecules, and also between vibrational nuclei motions and translational ones of molecules in a solid C_{60}, which is difficult to detect by using other effects at low temperature. Besides, a comparison of the values $T_{\mu\mu}$ (19) and $T_{\mu\mu}^{kk'}$ (27), obtained experimentally from the data of measuring the SLR time at different magnetic field orientations, can be used for determining the lattice parameter of a fullerene crystal C_{60}.

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СПІН-ГРАТКОВА РЕЛАКСАЦІЯ У ФОТОЗБУДЖЕНОМУ ТРИПЛЕТНОМУ СТАНІ ФУЛЕРИТУ С60: РОЗГЛЯД СПІН-ОРБІТАЛЬНОЇ ВЗАЄМОДІЇ

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Досліджено механізм спін-граткової релаксації (СГР) у фотозбуджених триплетних станах кристала фулерену С60, що зумовлений модуляцією енергії спін-орбітальної взаємодії (СОВ). Ця модуляція виникає як результат примішування обертальних рухів та коливальних рухів ядер молекули до її трансляційних рухів при акустичних коливаннях гратки. З використанням методів атом-атомних потенціалів та молекулярних орбіталей (МО) отримані прості вирази ймовірності СГР для прямих однофононних процесів. Проаналізований вплив динамічного ефекту Яна-Теллера у молекулі С60 на величину ймовірності СГР. Проведено порівняння розрахункових значень часу СГР з наявними експериментальними величинами.