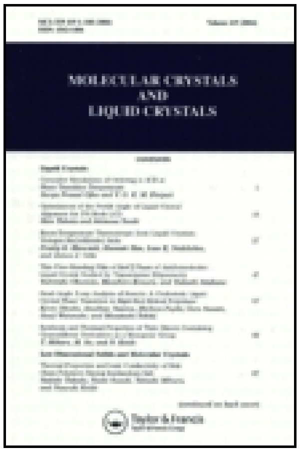

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of Spin-Lattice Relaxation in the Excited Triplet States of Impurity Molecular Crystals Induced by the Translational Molecule Motions and Intramolecular Nuclei Vibrations

V. A. Andreev [a] & YU. I. Prilutski [a]

[a] Department of Physics, Kiev Shevchenko University, Vladimirskaya St., 64, Kiev, 252 033, Ukraine

Version of record first published: 04 Oct 2006

To cite this article: V. A. Andreev & YU. I. Prilutski (1997): Investigation of Spin-Lattice Relaxation in the Excited Triplet States of Impurity Molecular Crystals Induced by the Translational Molecule Motions and Intramolecular Nuclei Vibrations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 307:1, 205-210

To link to this article: http://dx.doi.org/10.1080/10587259708047097

Mol. Cryst. Liq. Cryst., 1997, Vol. 307, pp. 205–210
Reprints available directly from the publisher
Photocopying permitted by license only

Investigation of Spin-Lattice Relaxation in the Excited Triplet States of Impurity Molecular Crystals Induced by the Translational Molecule Motions and Intramolecular Nuclei Vibrations

V. A. ANDREEV and YU. I. PRILUTSKI

Department of Physics, Kiev Shevchenko University, Vladimirskaya St., 64, Kiev, 252 033 Ukraine

(Received 26 July 1995; In final form 28 February 1997)

Direct one-phonon processes of spin-lattice relaxation are investigated in the excited triplet states of molecular crystals in high magnetic fields and at low temperatures. The mixing of the vibrational motions of the nuclei with the translational ones of the molecule is chosen as the major phenomenon, leading to the coupling between the spin system and acoustic vibrations. The angular, field and temperature dependences of the spin-lattice relaxation rate for an isotopic impurity in deuterobenzophenone crystal are calculated by the molecular orbitals and atom–atom potential methods.

Keywords: Triplet state; spin-lattice relaxation; atom–atom potentials; molecular orbitals

1. INTRODUCTION

The mixing of the translational and rotational (TRM) motions of the molecule and presence of the anisotropic spin–spin interactions is due to the known TRM relaxation mechanism in organic crystals [1–3]. Displacements of the nuclei can also induce the spin-lattice relaxation (SLR) as they change the electron density intramolecular distributions and modulate the components of fine-structure (FS) tensor [4].

Here we continue our previous investigation [3] of low-temperature SLR mechanisms in the organic molecular crystals. In the case of an isotopic impurity in the deuterobenzophenone crystal the SLR rates induced by the mixing of the vibrational motions of the nuclei with the translational motions of the molecule have been calculated without using any fitting parameters. The angular, field ($\vec{B}$) and temperature (T) dependences of SLR probability for the direct one-phonon processes were studied by the methods of molecular orbitals (MO) [5] and atom–atom potentials of intermolecular interactions [6]. The SLR rates due to the TRM relaxation mechanism [3] and the considered relaxation model are compared.

2. CALCULATION OF SLR PROBABILITIES

Consider the triplet excited impurity molecule (IM) in an organic molecular crystal. The crystal is located in a magnetic field $\vec{B}$. Assume that the spin energy in this field exceeds considerably the FS energy, so spin sublevels can be classified by the spin projection σ on the magnetic field. Let us investigate the probabilities of relaxation transitions between the triplet IM sublevels.

The starting point of our calculation is the fact, that the FS of EPR spectrum of the excited triplet IM depends on the electron density distribution and is defined by the dipole–dipole interaction of magnetic moments. According to the results [4] the spin-phonon interaction Hamiltonian is given by

$$H = \sum_{p}\sum_{\mu} \frac{\partial H_{FS}}{\partial R_{p\mu}} \delta R_{p\mu}(t), \tag{1}$$

where $\delta R_{p\mu}(t)$ is the displacement of pth nucleus in the field of an acoustic wave (μ denotes the X, Y and Z molecular axes):

$$\delta R_{p\mu}(t) = \sum_{\vec{f} j} \left[\frac{\hbar}{2N M_p \omega_{\vec{f} j}} \right]^{1/2} e_{p\mu}(\vec{f} j)[q^{+}_{\vec{f} j} \exp(i\omega_{\vec{f} j} t) + h.c.] \tag{2}$$

Here N is the number of the unit cells in the crystal; M_p is the mass of the pth nucleus of IM; $e_{p\mu}(\vec{f} j)$ is the μth component of the amplitude displacement for the pth nucleus of IM; $q^{+}_{\vec{f} j}$ is the phonon creation operator of the jth acoustic branch; $\vec{f}$ is the phonon wave vector; $\omega_{\vec{f} j}$ 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 $Z||\vec{B}$. Then the spin-phonon interaction Hamiltonian (1) can be rewritten as [4]

$$H=\sum_{p}\sum_{\mu}\sum_{M} T_M^2 P_{p\mu}^M \delta R_{p\mu}(t), \tag{4}$$

were T_M^2 is an irreducible tensor operator [7].

In the principal coordinate system of IM the non-zero values of constants $P_{p\mu}^M$ are equal to:

$$P_{p\mu}^{\pm 2}=3Z_{ef}(g\beta e)^2 \sum_{j\neq i} \frac{\langle j|R_{p1\mu}/R_{p1}^3\,|i\rangle}{E_i-E_j}\left\langle j\left|\frac{y_{12}^2-x_{12}^2}{r_{12}^5}\right|i\right\rangle \tag{5}$$

$$P_{p\mu}^{0}=\sqrt{6}\,Z_{ef}(g\beta e)^2 \sum_{j\neq i} \frac{\langle j|R_{p1\mu}/R_{p1}^3\,|i\rangle}{E_i-E_j}\left\langle j\left|\frac{r_{12}^2-3z_{12}^2}{r_{12}^5}\right|i\right\rangle$$

Here Z_{ef} is the effective charge of the carbon atom's nucleus; $R_{p1}=|\vec{R}_p-\vec{r}_1|$, where $\vec{R}_p$and $\vec{r}_1$ are the radius-vectors of the pth nucleus of the carbon atom and the first π-electron correspondingly; $|j>$ is the wave function and E_j is the energy of the triplet state of the excited IM. Equal contributions from both π-valence electrons have been accounted in (5). Matrix elements in (5) were calculated by *MO* method [4, 5].

Regarding the operator (4) as a perturbation we calculate the transition probability between IM spin sublevels with projections σ and $\sigma'(\sigma,\sigma'=0,\ \pm 1)$

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

where

$$A_{p\mu}^{M}=\sum_{M'} D_{MM'}^2\,P_{p\mu}^{M'} \tag{7}$$

Here $D_{MM'}^2$ are Wigner functions [7] that describe the orientation of $\vec{B}$ with respect to the equilibrium position of the IM molecular axes.

The dependence of relaxation transition rates on T and $\vec{B}$ is given by the correlation function $I_{\mu\nu}^{pp'}(\omega)$:

$$I_{\mu\nu}^{pp'}(\omega)=\int_{-\infty}^{+\infty}\langle\delta R_{p\mu}(t)\,\delta R_{p'\nu}(0)\rangle_T\,\exp(i\omega t)\,dt \tag{8}$$

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

Exact data on the constants that characterize the lattice dynamics of a real crystal with account of IM influence are required to calculate the correlation function (8). However, the data on the ideal crystal lattice dynamics can be used for the isotopic IM at the frequencies considerably less than the limiting frequency of acoustic phonons or for IM with insignificant variation of the force constants in comparison with the force constants of a perfect crystal [1]. Thus for the correlation function $I_{\mu\nu}(\omega)$ we have

$$I_{\mu\nu}^{pp'}(\omega)=\frac{\hbar V_0}{2\pi}T_{\mu\nu}^{pp'}\omega^5\left[1-\exp\left(-\frac{\hbar\omega}{kT}\right)\right]^{-1}, \tag{9}$$

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

$$T_{\mu\nu}^{pp'}=[M_p M_{p'}]^{-1/2}\sum_j\langle e_{p\mu}(\vec{f}j)e_{p'\nu}(\vec{f}j)f^{-4}v_{\vec{f}j}^{-7}\rangle_{\vec{f}} \tag{10}$$

Averaging in (10) is performed over all possible orientations of $\vec{f}$.

The values of $T_{\mu\nu}^{pp'}$ are found from the equations of lattice dynamics in the longwave approximation ($\vec{f}\to 0$), where coupling of the translational motions of the molecule and the intramolecular vibrations of the nuclei can be accounted for by the perturbation theory [3, 4].

The values of $T_{\mu\nu}^{pp'}$ for an benzophenone impurity in solid deuterobenzophenone were calculated by the method of atom–atom potentials [6] with the data on molecular crystal structure [8, 9]. The calculation has shown that the $T_{YY}^{pp'}$ elements dominate by two or three orders over the other ones. Here Y corresponds to the long molecular axis.

The results of numerical analysis of the parameters $T_{YY}^{pp'}$ allow to simplify the expressions for the SLR probabilities

$$W_{10}=a\omega^5\left[1-\exp\left(-\frac{\hbar\omega}{kT}\right)\right]^{-1}\sin^2 2\varphi \tag{11}$$

$$W_{1-1}=b(2\omega)^5\left[1-\exp\left(-\frac{2\hbar\omega}{kT}\right)\right]^{-1}(1+1.6\sin^2 2\varphi+0.6\sin^4\varphi),$$

where φ is the angle between $\vec{B}$ and the long molecular axis. The constants of spin-phonon coupling for an isotopic IM in the deuterobenzophenone crystal are equal to: $a=5.2*10^{-60}\,s^4$ and $b=1.3*10^{-59}\,s^4$.

3. DISCUSSION

Let us compare the obtained results between the TRM relaxation mechanism [3] and the current relaxation model.

The SLR rates in the TRM and current relaxation mechanisms have different angular dependences. Consequently the relaxation processes can be investigated by the selective way for both mechanisms. For example, only probabilities of transition W_{10} in the TRM mechanism [3] and W_{1-1} in the current one are different from zero at the orientation of magnetic field $\vec{B}$ along the molecular axis $Y(\varphi = 0)$.

The SLR rates in the TRM and current relaxation mechanisms have the same temperature dependence and the different magnetic field one: $W = a_1 B + a_3 B^3 + a_5 B^5$ for the TRM relaxation mechanism (a_1, a_3 and a_5 are the constants of the spin-phonon coupling [3]) and $W \sim B^5$ for the current model. It is allows to investigate the relaxation processes in the different regions of the magnetic field for both SLR mechanisms.

Obtained values of relaxation transition probability W_{10} at various T and B are given in Table. It is convenient to compare values of W_{10} for the current relaxation mechanism and the TRM mechanism for an angle $\varphi = \pi/4$ (since we have $W_{10} \sim \sin^2 2\varphi$ for the current model and $W_{10} \sim \cos^2 \varphi$ for the TRM mechanism [3]). The numerical analysis has shown that the contribution of current mechanism to the SLR is considerably less as compared with the TRM mechanism for the considered triplet excited system. This difference may be explained as follows. The SLR rates

TABLE I Values of the SLR probability W_{10} for different magnetic fields and temperatures: 1 – the current mechanism of SLR; 2 – the TRM mechanism of SLR [3]

SLR mechanisms	W_{10}, s^{-1}		
	B = 1 T	*5 T*	*10 T*
		$T = 1\ K$	
1	$7.6*10^{-4}$	2.3	$7.1*10^{1}$
2	0.8	$4.6*10^{1}$	$4.5*10^{2}$
		$T = 4.2\ K$	
1	$1.5*10^{-3}$	2.4	$7.2*10^{1}$
2	2.3	$0.7*10^{2}$	$4.9*10^{2}$
		$T = 10\ K$	
1	$0.3*10^{-2}$	3.0	$7.6*10^{1}$
2	5.1	$1.1*10^{2}$	$0.7*10^{3}$

in the TRM mechanism are in inverse ratio to the fourth power of the frequency of librational vibrations for the deuterobenzophenone crystal: $W^{\mathrm{TRM}} \sim 1/\omega_{\mathrm{lib}}^4$ [3]. The SLR rates in the current mechanism are in inverse ratio to the fourth power of the frequency of intramolecular vibrations for the IM in the deuterobenzophenone crystal: $W \sim 1/\omega_{\mathrm{vib}}^4$ [4]. Since $\omega_{\mathrm{lib}} \ll \omega_{\mathrm{vib}}$ [10–11], we have $W^{\mathrm{TRM}} \gg W$.

The obtained SLR probabilities carry information on lattice dynamics, in particular, information on the coupling between the vibrations of the nuclei and the translations of the molecules, which is difficult to detect using other effects.

Acknowledgement

This work was supported, in part, by a Soros Foundation Grant awarded by the American Physical Society.

References

[1] V. I. Sugakov and Yu. D. Shtepa, *Phys. Stat. Sol.*, (b), **116**, 633 (1983).
[2] V. A. Andreev and Yu. I. Prilutski, *Ukrainski Fiz. Zh.*, **37**, 844 (1992).
[3] V. A. Andreev and Yu. I. Prilutski, *Mol. Cryst. Liq. Cryst.*, **289**, 255 (1996).
[4] V. A. Andreev and Yu. I. Prilutski, *Fiz. Tverd. Tela (Phys. Sol. St.)*, **34**, 2204 (1992).
[5] S. Fuzinaga, The molecular orbitals method (Mir, Moscow, 1983).
[6] A. I. Kitaygorodski, Molecular crystals (Academic Press, 1973).
[7] D. A. Varshalovich, A. N. Moskalev and V. K. Hersonski, Quantum theory of angular momentum (World Scientific Publ. Co., Singapore, 1987).
[8] E. B. Fleisher, N. Sung and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).
[9] M. Stone, *Z. Naturf.* **36a**, 909 (1981).
[10] P. Ranson, P. Peretti, Y. Rousset and J. A. Koningstein, *Chem. Phys. Lett.*, **16**, 396 (1972).
[11] T. Kolev, B. Nikolova, B. Jordanov and I. Yuchnovski, *J. Mol. Struct.*, **129**(1) (1985).