Theory of the action of an acoustic wave on the phosphorescence spectrum of triplet-excited impurity centers in organic molecular crystals

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The acousto-phosphorescent double resonance is investigated within the context of the spin–phonon interaction caused by the coupling between the translational and rotational motions. This phenomenon consists of the following: the passage of an acoustic wave through a crystal causes the absorption of phonons with simultaneous transition between the spin sublevels of the triplet-excited state. Concomitant with this a change takes place in the relative populations of the spin sublevels, manifested in a change in the intensity and decay time of the detected phosphorescence spectrum. Numerical values have been obtained for the probability of direct single-phonon transitions for an isotopic impurity in a crystal of deutero-naphthalene both in strong magnetic fields and in zero field. A detailed analysis of the dependence of the transitions on the direction of propagation of the acoustic wave has also been carried out.

Because of the strong anisotropy of the intermolecular interactions in organic molecular crystals, translational motions are accompanied by a simultaneous rotation of the molecules about their axes, i.e., mixing of the translational and rotational motions takes place (translational-rotational mixing—TRM). The TRM mechanism allows the interaction energy of the fine structure of the spin sublevels to be modulated by the acoustic phonons and is the main source of low-temperature spin-lattice relaxation (SLR).[1]

Sugakov[2,3] has proposed the TRM mechanism as the explanation for the experimentally observed[4,5] acousto-phosphorescent double resonance (APDR). This phenomenon arises because the passage of an acoustic wave in the crystal causes the absorption of phonons with simultaneous transition between the spin sublevels of the triplet-excited state. Hence the relative populations of the spin sublevels change, which is manifested in a change in the intensity and decay time of the detected phosphorescence from the triplet levels of the impurity molecule. In the present paper we have continued the development of the theory of APDR for the case of an isotopic impurity in a crystal of deutero-naphthalene. We have obtained numerical values of the probabilities of the corresponding transitions for direct first-order processes. A distinguishing feature of this paper is a detailed analysis of the spin-phonon coupling mechanism and the dependence of the transition rates on the direction of propagation of the acoustic wave.

The spin Hamiltonian of the triplet-excited impurity molecule has the form

$$H_S=H_Z+H_{FS}, \tag{1}$$

where the operator

$$H_Z=g\beta\mathbf{HS} \tag{2}$$

describes the Zeeman interaction of the total spin of the electrons of the triplet-excited impurity molecule ($S=1$) with the stationary magnetic field $\mathbf{H}$, g is the spectroscopic splitting factor, β is the Bohr magneton,

$$H_{FS}=\sum_{\mu,\nu}D_{\mu\nu}S_\mu S_\nu \tag{3}$$

is the electron spin Hamiltonian in zero field, which gives rise to the fine structure of the EPR spectra, expressed in terms of the components of the electron spin S_μ and the components of the fine-structure tensor $D_{\mu\nu}$. In the system of principal axes of the molecule the quantities $D_{\mu\nu}$ are expressed in terms of the two fine-structure constants D and E (Ref. 6):

$$D_{xx}=E-{}^1/_3D,\ D_{yy}=-E-{}^1/_3D.\ D_{zz}={}^2/_3D. \tag{4}$$

Let us assume that a plane monochromatic acoustic wave of the jth branch with wave vector $\mathbf{f}$ and frequency $\omega_{\mathbf{f}j}$ equal to the frequency of the transition between certain spin states of the excited impurity center, and significantly smaller than the Debye frequency, propagates in the crystal. The interaction of the spin system with the acoustic wave arises as a consequence of changes in the components of the fine-structure tensor during rotations of the molecules caused by displacement of their centers of mass. This interaction is described by the Hamiltonian[1]

$$\delta H_{FS}=\sum_{\mu,M}T_M{}^2\Pi_\mu{}^M\theta_\mu(t). \tag{5}$$

Here T_M^2 are polarization operators,[7] written in a coordinate system whose z axis is aligned with the magnetic field vector $\mathbf{H}$; Π_μ^M are constants whose nonzero values are linear combinations of the fine structure constants:

$$\Pi_x{}^{\mp1}=i(D+E),\ \Pi_y{}^{\mp1}=\mp(D-E),\ \Pi_z{}^{\mp2}=\mp2iE, \tag{6}$$

$\theta_\mu(t)$ is an infinitesimal rotation angle about the μth molecular axis:

$$\theta_\mu(t)=\left(\frac{\Pi V_0}{I_\mu v_{\mathbf{f}j}}\right)^{1/2}\frac{e_\mu(\mathbf{f}j)}{\omega_{\mathbf{f}j}}\cdot[\exp(-i\omega_{\mathbf{f}j}t)+\text{c.c.}], \tag{7}$$

where Π is the magnitude of the acoustic energy flux, V_0 is

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the volume of the unit cell of the crystal, I_μ is the μth component of the moment of inertia of the molecule, v_{fj} is the phase velocity, and $e_\mu(\mathbf{f}j)$ is the μth component of the polarization vector.

We will analyze the APDR phenomenon in two limiting cases, namely in the approximation of strong magnetic fields ($g\beta H \gg D,E$) and in zero field ($H=0$).

In the strong-field approximation the probability of transitions between the triplet sublevels σ and σ' ($\sigma,\sigma' = 0, \pm 1$) caused by perturbation (5) and accompanied by absorption of a phonon is equal to

$$W_{\sigma\sigma'} = \frac{\pi V_0 \Pi}{\hbar} |\sigma-\sigma'| \sum_{\mu,\nu} T_{\mu\nu}(\mathbf{f}j) A_\mu^{\sigma-\sigma'} \bar{A}_\nu^{\sigma-\sigma'} \rho(\hbar\omega_{\sigma\sigma'}), \tag{8}$$

where

$$T_{\mu\nu} = (I_\mu I_\nu)^{-1/2} e_\mu(\mathbf{f}j) e_\nu(\mathbf{f}j) f^{-2} v_{\mathbf{f}j}^{-3}, \tag{9}$$

$$A_\mu^M = \sum_\gamma D_{M\gamma}^2 \Pi_\mu^\gamma, \tag{10}$$

$D^2_{M\gamma}$ are Wigner functions[7] which describe the orientation of the magnetic field vector with respect to the equilibrium position of the molecular axes, $\rho(\hbar\omega)$ is the line shape function, and ω is the Larmor frequency.

In the case of zero field we have

$$W_{\sigma\sigma'} = \pi V_0 \Pi \hbar \omega^2_{\sigma\sigma'} T_{\mu\mu}(\mathbf{f}j) \rho(\hbar\omega_{\sigma\sigma'}), \tag{11}$$

where σ, σ', and μ are distinct values of the indices x, y, and z that label the molecular axes. The transition energies at $H=0$ are equal to

$$\hbar\omega_{xy} = D-E,\ \hbar\omega_{yz} = D+E,\ \hbar\omega_{xz} = 2E. \tag{12}$$

The values of the parameters $T_{\mu\nu}$ figuring in formulas (8) and (11) were found in the dipole limit ($\mathbf{f}\to 0$), in which the coupling between the translational and rotational motions of the molecules can be accounted for by perturbation theory, which makes it possible to establish a connection between the quantities $T_{\mu\nu}$, which describe translational-rotational mixing, and the elements of the dynamic matrix of the crystal v^{rt}:

$$T_{\mu\nu} = (I_\mu I_\nu)^{-1/2} \sum_{\lambda,\lambda'} \frac{u_{\lambda\mu} u_{\lambda'\nu}}{\omega_{0\lambda}^2 \omega_{0\lambda'}^2} \sum_j V_\lambda^{rt}(\mathbf{n}j) V_{\lambda'}^{rt}(\mathbf{n}j) v_j^{-3}(\mathbf{n}) \tag{13}$$

[the derivation of formula (13) is given in the Appendix].

For an isotopic impurity in a crystal of deutero-naphthalene the quantities $T_{\mu\nu}$ were calculated numerically using the method of atom-atom potentials[8] and results of molecular crystal dynamics calculations.[9] Here consideration was taken of the fact that for low values of the frequency the effects of the impurity molecule are insignificant,[10] and the use in the calculations of the results of lattice dynamics calculations for an ideal crystal is justified.

The presence of a symmetry center in the system under consideration leads to the result that only the diagonal elements of the matrix $T_{\mu\nu}$ are nonzero, i.e., T_{xx}, T_{yy}, and T_{zz}. However, numerical calculation has shown that the T_{xx} matrix element dominates. The other two are two to three orders of magnitude smaller.

Figure 1 plots the dependence of T_{xx} (isolines) on the direction of propagation of the acoustic wave in the crystal ($\tilde\theta$, $\tilde\varphi$ are the angles in the spherical coordinate system). As can be seen, the value of T_{xx} grows as $\tilde\theta$ increases and $\tilde\varphi$ decreases.

Analyzing the contributions of the different terms of formula (13), we find that the main contribution to T_{xx} comes from only one acoustic branch, the one whose polarization vector is parallel to the crystal axis **b** ($\mathbf{b}\|\mathbf{C}_2$). This branch is associated with librational vibrations, which are associated with rotation of the molecule about an axis close to its long axis of inertia.

The results of numerical analysis of the parameters $T_{\mu\nu}$, allow us to simplify the expressions for the transition probabilities. In the strong-field approximation we have

$$W_{10} = a\cos^2(2\varphi)\rho(\hbar\omega_{10}), \tag{14}$$

$$W_{1-1} = {}^1\!/_2 a \sin^2(2\varphi)\rho(\hbar\omega_{1-1}), \tag{15}$$

where

$$a = \pi V_0 T_0 (D+E)^2 \Pi/\hbar, \tag{16}$$

and φ is the angle between the magnetic field vector **H** and the long axis of the molecule. For a given acoustic-wave power $\Pi = 10^{-4}$ W/cm^2 and $T_0 = 5\cdot 10^6$ s^3/g$\cdot$cm^3 for a naphthalene impurity in a crystal of deutero-naphthalene we find $a = 2\cdot 10^{-18}$ g$\cdot$cm^2/s^3.

In zero magnetic field the transition between the y and z spin states dominates:

$$W_{yz} = a\rho(\hbar\omega_{yz}). \tag{17}$$

As can be seen, in this case rotation of the molecule about the long axis of inertia is responsible for the resonance.

We may use Eqs. (14), (15), and (17) to obtain a numerical estimate of the transition probabilities. For this pur-

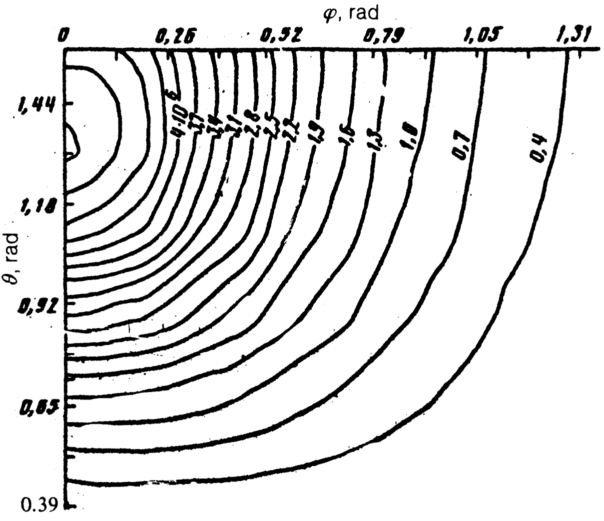

FIG. 1. Dependence of the magnitude of T_{xx} (isolines) on the orientation of the wave vector of the acoustic wave in a crystal of deutero-naphthalene with naphthalene impurity.

pose we set $\varphi = 0$ and $\rho(\hbar\omega) \sim 1/\hbar\Delta\omega$, where $\Delta\omega$ is the half-width of the EPR line: $\Delta\omega \sim 10^8$ s^{-1}. Finally we have $W_{10} = W_{yz} \sim 20$ s^{-1}.

Thus, in strong magnetic fields three lines (the Zeeman effect) are observed in the spectrum of a deutero-naphthalene crystal and in this case the APDR phenomenon consists of a redistribution of the intensities of these three lines. Consequently, there should exist three APDR frequencies. In the case of zero magnetic field the intensity of only one line changes significantly. Therefore only one APDR frequency should be observed.

The numerical values of the probabilities of the transitions between the triplet sublevels of the impurity center with absorption of a phonon obtained above are comparable with the probabilities of longitudinal relaxation and fluorescence of the triplet states of molecular crystals. This indicates that an acoustic wave can cause a marked redistribution of the populations of the spin states and, consequently, alter the phosphorescence spectrum. On the other hand, the APDR phenomenon can be helpful in the study of the coupling of the translational and rotational motions in a crystal, which is important for the identification of the TRM mechanism of the spin-phonon interaction.

APPENDIX. THE CALCULATION OF $T_{\mu\nu}$ BY PERTURBATION THEORY

Consider a crystal whose unit cell contains two molecules and which possesses a second-order symmetry axis C_2 and a symmetry center. We will represent the amplitude vector of the displacements of the molecules of the crystal in the form of a column vector in which the translational ($\mathbf{e}^t$) and rotational ($\mathbf{e}^r$) components are grouped, and we write the equations of motion of the lattice in the form

$$\begin{pmatrix} \hat{T} & \hat{V} \\ \hat{V}^+ & \hat{R} \end{pmatrix} \begin{pmatrix} \mathbf{e}^t \\ \mathbf{e}^r \end{pmatrix} = \omega^2 \begin{pmatrix} \mathbf{e}^t \\ \mathbf{e}^r \end{pmatrix}, \tag{18}$$

where $\hat{T}$, $\hat{R}$, and $\hat{V}$ are blocks of elements of the dynamic matrix which describe the elastic interactions during the translational and rotational motions of the molecules, and also during TRM.

One result of the presence of the indicated symmetry elements is that the dynamic matrix in the long-wave limit ($\mathbf{f} \to 0$) possesses the following properties:

$$\begin{gathered} \hat{T}(\mathbf{f}) = \hat{T}(0) + o(f^2), \\ \hat{R}(\mathbf{f}) = \hat{R}(0) + o(f^2). \\ \hat{V}(\mathbf{f}) = o(\mathbf{f}). \end{gathered} \tag{19}$$

Thus, for $\mathbf{f} = 0$ TRM is absent and the limiting values of the amplitude vectors divide up into two groups which describe pure translations and pure rotations. The components of these two vectors satisfy the equations

$$\hat{T}(0)\mathbf{e}_0{}^t = \omega^2 \mathbf{e}_0{}^t; \tag{20}$$

$$\hat{R}(0)\mathbf{e}_0{}^r = \omega^2 \mathbf{e}_0{}^r. \tag{21}$$

The three vectors $\mathbf{e}_0^t = \mathbf{e}_{ak,\alpha}^{t0}$, corresponding to the triply degenerate eigenvalue $\omega = 0$, can be chosen parallel to the crystal axes. The vectors $\mathbf{e}_0^t = \mathbf{e}_{\text{opt},\alpha}^{t0}$, $\omega = \omega_{0\ \text{opt},\alpha} \neq 0$, and $\mathbf{e}_0^r = \mathbf{e}_{\text{lib},\alpha}^{r0}$, $\omega = \omega_{0\ \text{lib},\lambda} \neq 0$, which describe the limiting values of the optical and librational vibrations, are calculated using Eqs. (20) and (21).

For $\mathbf{f} \neq 0$ TRM implies that the acoustic vibrations have rotational as well as translational components. Using the limiting values of the vectors and frequencies as a zeroth approximation and taking relations (18) and (19) into account, it is possible to find these components from perturbation theory. In the linear dispersion region their translational components do not contain any limiting optical phonons and are determined by the equation

$$[\hat{\Lambda}(\mathbf{n}) - v_j^2(\mathbf{n})]\mathbf{e}_{ak}{}^t(\mathbf{n}j) = 0, \tag{22}$$

in which $v_j(\mathbf{n})$ is the phase velocity of the j-branch phonon, propagating in the direction $\mathbf{n} = \mathbf{f}/|\mathbf{f}|$, defined by the condition that the determinant of Eq. (22) vanish, and

$$\hat{\Lambda}(\mathbf{n}) = \frac{\partial^2}{\partial f^2}[\hat{T}(\mathbf{f}) - \hat{V}(\mathbf{f})\hat{R}(\mathbf{f})\hat{V}(\mathbf{f})]\big|_{\mathbf{f}\to 0}. \tag{23}$$

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

$$\mathbf{e}_{ak}^r(\mathbf{n}j) = \sum_\lambda \mathbf{e}_{\text{lib},\lambda}^{r0} \frac{(\mathbf{e}_{\text{lib},\lambda}^{r0}, \hat{V}(\mathbf{f})\mathbf{e}_{ak}^t(\mathbf{n}j))}{\omega_{0,\text{lib},\lambda}^2}. \tag{24}$$

Introducing the notation $u_{\lambda\mu}$ for the projection of the limiting value of the amplitude vector of the λ th librational vibration onto the μth axis of the molecule and

$$V_\lambda{}^{rt}(\mathbf{n}j) = \frac{\partial}{\partial f}(\mathbf{e}_{lib,\lambda}^{r0}. \hat{V}(\mathbf{f})\mathbf{e}_{ak}{}^t(\mathbf{n}j))\big|_{\mathbf{f}=0},$$

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

$$e_\mu(\acute{\mathbf{f}}j) = f\sum_\lambda u_{\lambda\mu} V_\lambda{}^{rt}(\mathbf{n}j)\,\omega_{0\ lib,\lambda}^{-2}. \tag{25}$$

Substituting the given expression in Eq. (9), we arrive at the desired formula (13).

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