Relaxation processes in a pyrene-doped diphenyl crystal by the Dicke superradiance method

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With a pyrene-doped diphenyl crystal as an example (transition ^1B-^1A_g, wavelength 3793.3 Å), we investigate the effect of phonons on the onset of Dicke superradiance and demonstrate the extent to which this phenomenon can provide information on the relaxation parameters. The temperature dependence of the superradiance intensity at the maximum is investigated and explained for two values of the pyrene concentration in the diphenyl matrix (0.1 and 0.25 mol.%). This dependence yields the lifetimes τ_{phn} of the pseudolocalized phonon states and the activation energy ΔE of the phonons: $\tau_{\text{phn}} = 2$–20 ns and $\Delta E = 8 \pm 4\ \text{cm}^{-1}$ for $C = 0.1$ mol.% and $\tau_{\text{phn}} = 1$–15 ns and $\Delta E = 7 \pm 3\ \text{cm}^{-1}$ for $C = 0.25$ mol.%. The experimentally plotted spectra of light absorption for the 0–0 transition at two temperatures have confirmed the presence of vibrational sublevels through which Orbach relaxation proceeds.

Optical superradiance constitutes coherent narrow-directivity spontaneous emission of light by an ensemble of particles excited to a collective state; the intensity of this emission is proportional to the square of the number of particles.[1] Most earlier studies in gaseous media were devoted mainly to the distinguishing features of the evolution of this phenomenon in time and to its properties.[2] The first experiments on optical superradiance in doped crystals were performed recently.[3–6] Many fundamental problems concerning the evolution of this phenomenon have remained uninvestigated, particularly the role of the phonons in the dynamics of superradiance development at high crystal temperatures. It is furthermore of practical importance to assess the possibility of using this phenomenon to investigate relaxation processes and their parameters. The present paper is devoted to these problems.

We present below a detailed analysis of an experimentally plotted temperature dependence of superradiance in a diphenyl crystal containing pyrene molecules for the $^1B_{2u}$–^1A_g transition (wavelength $\lambda = 3739.9$ Å) of the latter. This analysis yielded the lifetimes of the pseudolocalized phonons and the activation energies for two values of the density of pyrene molecules in a diphenyl matrix at temperatures 1.6–4.2 K.

§1. TEMPERATURE DEPENDENCE OF THE INTENSITY OF THE DICKE OPTICAL SUPERRADIANCE IN A DIPHENYL CRYSTAL WITH PYRENE

We investigated in this experiment solid solutions of pyrene molecules in diphenyl. The diphenyl crystal belongs to the monoclinic space group $C_{2h}{}^5$ with two molecules per unit cell. The pyrene molecule is planar and belongs to the point group D_{2h}. Three types of center can be produced, with different probabilities, whereby the pyrene molecule occupies different positions in the diphenyl matrix. This leads to a multiplet structure of the spectral lines. In particular, the purely electronic transition line (0–0 transition), on which the superradiance takes place, is a "trident" with peaks of different height. A distinguishing feature of the energy spectrum of pyrene in diphenyl is that this crystal can be treated as a system with weak electron--phonon interaction (the intensities of the phonon wings are low both in absorption and in luminescence).

The structure of the working energy levels of pyrene in diphenyl is shown in Fig. 1a. Pumping was by a nitrogen laser on the 1–3 transition to one of the vibronic sublevels. The 3–2 nonradiative relaxation carries the excitation rapidly to state 2 ($^1B_{2u}$ level). It was shown experimentally in Refs. 3 and 4 that Dicke superradiance is realized on the 2–1 transition ($^1B_{2u} \rightarrow {}^1A_g$—0–0 transition). The crystal-excitation scheme is shown in Fig. 1b. The optimum conditions for the onset of superradiance in such as excitation geometry are produced only in the front part of the sample, whereas in the second part the superradiance pulse propagates in the self-induced transparency regime[7] (an analogous situation obtained also in the experiment of McGillivray and Feld,[8] who also concluded that account must be taken of the "reaction" of the medium to the formation of superradiance in an extended sample). In our experiment the sample length was 0.4 cm., and the optimum conditions for superradiance-pulse formation were reached at the length 0.15 cm. Since the allowance for the reaction of the medium is discussed in detail in preceding papers,[7,4] we confine ourselves in the theoretical analysis below mainly to the superradiance aspect of the problem.

Figure 2 shows the experimental[9] temperature dependences of the intensity of the optical superradiance (at the maximum) for two pyrene densities (a—0.25 mol.% and b—0.1 mol.%). As expected, the superradiance intensity falls with rising temperature, and the fall takes place in the same temperature interval as in the case of optical (photon) echo,[10,13] where the fall mechanism is determined by the

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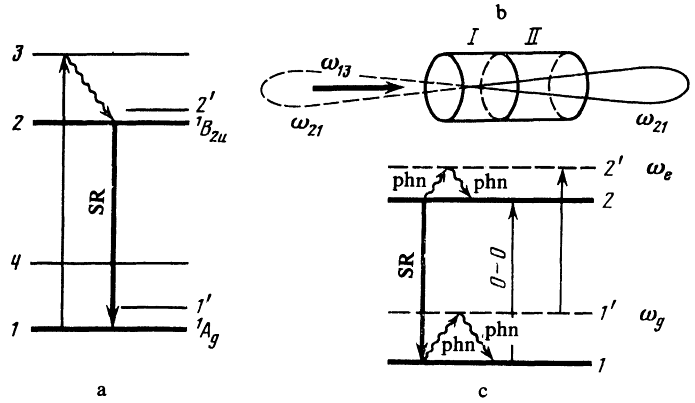

FIG. 1. a—Working-level scheme of pyrene in a diphenyl matrix when superradiance is produced; b—excitation scheme of diphenyl crystal with pyrene. I—crystal region where the superradiance is formed; II—crystal region where the superradiance pulse propagates in the self-induced transparency regime; c—level scheme that interprets the electron transitions to vibrational levels under the influence of pseudolocalized phonons (SR—superradiance; 0–0—$^1B_{2u} - {}^1A_g$; phn—phonon.

Orbach process with participation of pseudolocalized phonons, while the reciprocal of the time T_2 of the total dephasing consists of two components:

$$T_2^{-1}=(2T_1)^{-1}+[T_2'(T)]^{-1}, \tag{1}$$

where T_1 is the relaxation time of the upper-level nonequilibrium population, and $T_2'(T)$ is the time of pure phase relaxation defined in the case of the Orbach process by[10–13]

$$[T_2'(T)]^{-1}=[T_2'(0)]^{-1}+[T_2'(\infty)]^{-1}\exp(-\Delta E/kT),$$

where $T_2'(0)$ is the temperature-independent part of T_2' (under the condition of this experiment, the time $T_2'(0)$ due to the dipole-dipole interaction is not shorter than 10^{-7} s, so that the contribution of the corresponding term to T_2^{-1} in Eq. (1) can be neglected; $T_2'(\infty)$ is the phonon lifetime (which we designate also by τ_{phn}; ΔE is the energy gap between the ground or excited electron levels and the nearest vibrational level (this parameter is frequently called the activation energy).

According to Refs. 10–13, the optical dephasing in doped molecular crystals at liquid-helium temperature is due as a rule to relaxation transitions from the upper (e) or lower (q) electron energy levels to the vibrational sublevels, accompanied by energy absorption from pseudolocalized phonons (Fig. 1c). The impurity centers in these vibrational states execute librations (rotational rocking).[13] In the case of pyrene molecules, the maximum angles of these librations are given by the possible spatial orientations of the pyrene in the diphenyl matrix. The frequencies ω_q and ω_e of the libration oscillations about the ground and excited states are frequently different. It was shown in Ref. 12, in particular, that for such systems we have

$$[T_2'(T)]^{-1}$$
$$=\frac{1}{2}\left[\frac{1}{\tau_q}\exp\left(-\frac{\omega_q}{k_{\mathrm{B}}T}\right)+\frac{1}{\tau_e}\exp\left(-\frac{\omega_e}{k_{\mathrm{B}}T}\right)\right]+\Gamma^A_{(qe)}, \tag{3}$$

where τ_q and τ_e are the lifetimes of the vibrational sublevels near the ground (q) and excited (e) electronic levels; $\Gamma^A_{(qe)}$ describes the adiabtic contribution to the homogeneous line width, a contribution due to the two-phonon relaxation processes[14] (which is substantial at temperatures above 20 K).

Harris *et al.*[15,16] investigated the mechanisms and times of optical dephasing in localized and delocalized states of molecular crystals. It was shown that it is just the part, quadratic in the phonon operators, of the electron-phonon interaction Hamiltonian which is responsible for the temperature dependences of both the homogeneous width and the frequency shift in the optical spectrum. This conclusion is logical also from the physical viewpoint if account is taken of the short (picosecond) lifetime of the vibrational levels. Electrons that turn out to be acted upon by pseudolocalized phonons in one of the vibrational sublevels return rapidly to the initial electronic state and lose all their phase memory, i.e., two direct processes (Orbach relaxation) are realized in practice, while single (one-phonon) direct processes are less likely. This is indicated, in particular, also by the character of the experimentally plotted decrease with temperature.

Thus, in the theoretical exposition that follows it will also be assumed that the fall of the intensity of the Dicke superradiance with temperature in a diphenyl crystal with pyrene is connected with activation of the interaction of the unpaired pyrene molecules with the pseudolocalized phonons and is caused by the part, quadratic in the phonon operators, of the Hamiltonian of this interaction. From these decreases we shall determine, at two concentrations of the impurity molecules, the characteristics of these phonons, after which we shall corroborate spectroscopically the assumption that they exist.

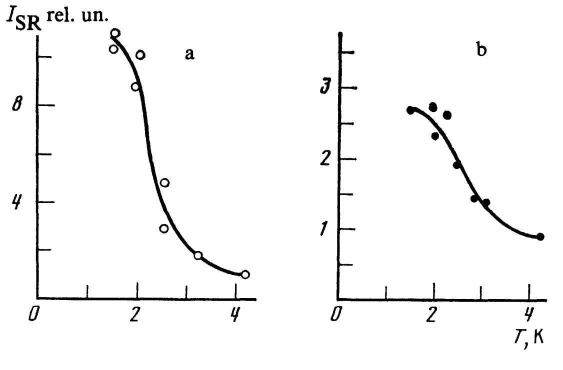

FIG. 2. Temperature dependence of the intensity of optical superradiance at the maximum for two densities of the pyrene molecules in the diphenyl matrix: a—0.25 mol.%; b—0.1. mol.%.

§2. THEORETICAL ANALYSIS OF THE TEMPERATURE FALLS OF THE DICKE SUPERRADIANCE INTENSITY

The Hamiltonian of the system, with allowance for its interaction with the field of the photons (pht) and phonons (phn), can be represented in the form

$$H=H_{\mathrm{s}}+H_{\mathrm{pht}}+H_{\mathrm{phn}}+H_{\mathrm{s-pht}}+H_{\mathrm{s-phn}}=H_0+H_1, \tag{4}$$

where

$$H_0=H_{\mathrm{s}}+H_{\mathrm{pht}}+H_{\mathrm{phn}} \quad H_1=H_{\mathrm{s-pht}}+H_{\mathrm{s-phn}} \quad H_{\mathrm{s}}=\hbar\sum_j^N \omega_0{}^j S_j{}^z$$

is the energy operator of the system of impurity molecules in the two-level model described by the energy spin $S=\frac{1}{2}$; S^z is the longitudinal component of the energy spin operator; $\hbar$ is Planck's constant; ω_0^j is the frequency of the energy transition between the working electron levels of the jth impurity centers;

$$H_{\mathrm{pht}}=\sum_{\mathbf{k},\sigma} \hbar\omega_k a_{k\sigma}{}^+ a_{k\sigma}$$

is the energy operator of the field of the transverse photons; $a_{\mathbf{k}\sigma}{}^+$ and $a_{\mathbf{k}\sigma}$ are the creation and annihilation operators for photons with wave vector **k** and polarization σ; $\omega_{\mathbf{k}}$ is the frequency of the photons of mode **k**;

$$H_{\mathrm{phn}}=\sum_{q,\alpha} \hbar\Omega_q b_{q\alpha}{}^+ b_{q\alpha}$$

is the energy operator of the phonon field; $b_{q\alpha}^+$ and $b_{q\alpha}$ are the creation and annihilation operators of phonons with wave vector **q** and polarization α; Ω_q is the frequency of the phonons of mode **q**;

$$H_{\mathrm{s-pht}}=\sum_j \sum_{k,\sigma} [g_{k\sigma} \exp(i\mathbf{k}\mathbf{r}_j) S_j{}^+ a_{k\sigma}+\mathrm{H.c.}$$

is the electron-phonon interaction operator; $g_{k\sigma}$ is the interaction constant of the impurity electron with a photon having parameters **k** and σ; $\mathbf{r}_j$ is the radius vector of the location of the jth impurity of the molecule that interacts with the photons; $S^+=S^x+iS^y$, where S^x and S^y are the transverse components of the energy spin; H.c. stands for the Hermitian-conjugate term;

$$H_{\mathrm{s-phn}}=\frac{1}{2}\sum_j \sum_{q,q',\alpha} \{\varphi_{j\alpha}(q,q') b_{q\alpha}{}^+ b_{q'\alpha}+\varphi_{j\alpha}{}^*(q,q') b_{q\alpha} b_{q'\alpha}^+\} S_j{}^z \tag{5}$$

is the interaction Hamiltonian of the impurity-center electron with the pseudolocalized phonons; $\varphi_{j\alpha}$ is the electron-phonon coupling constant:

$$\varphi_{j\alpha}(q,q')=\varphi_{j\alpha}{}^*(q',q).$$

Expression (5) could contain in principle the single-phonon spin-lattice relaxation Hamiltonian (corresponding to the direct process):

$$\sum_j \sum_{q,\alpha} h_{jq\alpha}(b_{q\alpha}{}^+ + b_{-q\alpha}) S_j{}^z \tag{6}$$

(where $h_{jq\alpha}$ is the electron-phonon interaction constant of this relaxation mechanism), with the relaxation corresponding as a rule to the case of strong electron-phonon coupling (in molecular crystals). In an electronic transition this case is accompanied by lattice deformation, and the molecules can be considered as oscillating about new equilibrium positions. In the diphenyl crystal, however, as already noted in §1, the electron-phonon coupling is weak. Therefore the single-phonon part of the Hamiltonian $H_{\mathrm{s-phn}}$ will hereafter be neglected. That part of this Hamiltonian which is quadratic in the phonon operators describes impurity-electron transitions, induced by phonons pseudolocalized phonons, to vibrational levels, and the inverse transitions (the Orbach process). Thus, on the one hand, a correlation in the molecule emission will be produced through the radiation field which is common to all of them, but on the other hand this correlation will be destroyed with rising temperature because the pseudolocalized phonons cause loss of phase information in the Orbach process.

To find an equation that describes the dynamic of the superradiant decay of excited electronic states under conditions when pseudolocalized phonons are activated, we use Zubarev's nonequilibrium-statistical-operator method.[17] We consider the system for times $t \geqslant \tau_{32}=\tau_{41}=10^{-12}$ s and introduce the following quasi-integrals of motion that correspond to the Hamiltonian (4):

$$R_z=2\sum_{j=1}^N S_j{}^z,$$

$$R_{\mathbf{k}_0}{}^2=\sum_{i,j}\left\{\frac{1}{2}[S_i{}^+ S_j{}^- \exp(i\mathbf{k}_0\mathbf{r}_{ij}) + S_i{}^- S_j{}^+ \exp(-i\mathbf{k}_0\mathbf{r}_{ij})]+S_i{}^z S_j{}^z\right\}, \tag{7}$$

where $\mathbf{r}_{ij}$ is the radius vector that joins the ith and jth molecules; $\mathbf{k}_0$ is the wave vector of a certain averaged mode corresponding to the wave packet, since $[R_z, H_0]_-=[R_{k0}{}^2, H_0]_-=0$. It was shown in Ref. 4 that under the conditions of our experiment the superluminescence process is not dominant. Neglecting the enhancement of the spontaneous emission in second-order perturbation theory in H_1 (Ref. 18), we obtain the following transport equations:

$$\frac{d\langle R_z\rangle}{dt}=\hbar^{-2}\int_{-\infty}^0 dt\, e^{\varepsilon t}\langle[H_1(t),[R_z,H_1]_-]_-\rangle_q, \tag{8}$$

$$\frac{d\langle R_{\mathbf{k}_0}{}^2\rangle}{dt}=\hbar^{-2}\int_{-\infty}^0 dt\, e^{\varepsilon t}\langle[H_1(t),[R_{\mathbf{k}_0}{}^2,H_1]_-]_-\rangle_q, \tag{9}$$

where

$$H_1(t)=\exp(i\hbar^{-1}H_0t)H_1\exp(-i\hbar^{-1}H_0t),$$

$\langle\ldots\rangle_q$ denotes averaging over the quasi-equilibrium operator

$$\rho_q=Q_q{}^{-1}\exp\left\{-\sum_m \beta_m D_m\right\}, \quad Q_q=\mathrm{Sp}\left\{\exp\left[-\sum_m \beta_m D_m\right]\right\}; \tag{10}$$

here β_m are the reciprocal temperatures of the D_m subsystems (R_2,$R_{\mathbf{k}_0^2}$, n_{pht}, n_{phn}). In the general case, in accordance with the method of nonequilibrium statistical operators,[17] the nonequilibrium mean values for the quasi-integrals of motion coincide with their quasi-equilibrium mean values, i.e., for example, $\langle R_z \rangle = \langle R_z \rangle_q$ and $\langle R_{k0}{}^2 \rangle = \langle R_{k0}{}^2 \rangle_q$ (Ref. 17). Carrying out in (8) the transformations, in the approximation of spatially homogeneous inversion, for a cylindrical sample, we obtain the following equation for $\langle R_z \rangle$ under the assumption that only the interaction with one dispersionless phonon mode of frequency is important:

$$\frac{d^2\langle R_z\rangle}{dt^2} = \left[\frac{\mu}{T_1}\langle R_z\rangle - \frac{1}{T_1} - \frac{1}{T_2'(T)}\right]\frac{d\langle R_z\rangle}{dt} + \frac{1}{T_1}\left[\frac{\mu}{T_1'}\langle R_z\rangle - \frac{1}{T_2'(T)}\right](\langle R_z\rangle + N), \tag{11}$$

where the form factor is

$$\mu = 2\hbar^{-2}\pi T_1 \sum_{\mathbf{k}} |g_k|^2 \Gamma(\mathbf{k}-\mathbf{k}_0)\,\delta[\omega_0 + \hbar^{-1}\langle\xi\rangle - \omega_k],$$

and

$$\Gamma(\mathbf{k}-\mathbf{k}_0) = \left| N^{-1} \sum_j \exp[i(\mathbf{k}-\mathbf{k}_0)\mathbf{r}_j \right|^2,$$

$$\langle\xi\rangle = {}^1/_2 \sum_q \varphi_{qq}(2\langle b_q{}^+ b_q\rangle + 1).$$

For a cylindrical sample we have for large Fresnel numbers[2] $\mu = 3\lambda^2/8\pi S$ and $S \gg (\lambda/2\pi)^2$, $L < S/\lambda$, where S is the sample cross section, λ the working wavelength, and L the sample length. Equation (11) contains also the parameters

$$\frac{1}{T_1'} = \frac{(1-\mu)}{T_1}, \quad \frac{1}{T_1} = \frac{1}{\tau_0}\left[1 + \alpha \,\mathrm{cth}\,\frac{\hbar\Omega_0}{2k_B T}\right]. \tag{12}$$

Here $1/T_1$ is the probability of spontaneous emission of an isolated impurity center for a finite lattice temperature (with account taken of the electron-phonon interaction via the considered transition);

$$\alpha = \frac{1}{2\hbar\omega_0}\sum_q \varphi_{qq}; \quad \frac{1}{\tau_0} = 2\pi\hbar^{-2}\sum_k |g_k|^2 \delta(\omega_0 - \omega_k);$$

is the time of spontaneous decay of an isolated impurity center[2]; in addition,

$$\frac{1}{T_2'(T)} = \frac{1}{4}\beta \,\mathrm{cosech}^2\left(\frac{\hbar\Omega_0}{2k_B T}\right), \quad \beta = \frac{2\pi}{\hbar^2}\sum_{q\neq q'} (\delta\varphi_{qq'})^2; \tag{13}$$

$$(\delta\varphi_{qq'})^2 = \frac{1}{N(N-1)}\sum_{i\neq j} (\overset{j}{\varphi}_{qq'}\overset{i}{\varphi}_{q'q} - \overset{i}{\varphi}_{qq'}\overset{j}{\varphi}_{q'q}), \tag{14}$$

where $T_2'(T)$ is the time of pure phase relaxation as a function of temperature. We shall neglect here and elsewhere the contribution to the transverse relaxation from the emission into the lateral modes and from the dipole-dipole interaction. It was assumed above that the phonons have an equilibrium distribution in the crystal, i.e., that the average number of the phonons of frequency Ω_0 is

$$n(\Omega_0) = \langle b_{q_0}{}^+ b_{q_0}\rangle = \left\{\exp\left(\frac{\hbar\Omega_0}{k_B T}\right) - 1\right\}^{-1}, \tag{15}$$

where $\mathbf{q}_0$ is the wave vector of the phonons of frequency Ω_0. For low temperatures (i.e., at $\hbar\Omega_0/k_B T \gg 1$) we have

$$\frac{1}{T_2'(T)} \approx \beta \exp\left(-\frac{\hbar\Omega_0}{k_B T}\right). \tag{16}$$

If superradiance is produced in the system, the change of $d\langle R_z\rangle/dt$ is of the order of $(\langle R_z\rangle + n)/\tau_s$, where $\tau_s = \mu N/T_1$ is the self-induction time of the correlations.[2] Since $1/\tau_s \gg 1/T_1$ under the conditions of our experiment, the term $(\langle R_z\rangle + N)/T_1 T_2'$ in (11) will be smaller than $(1/T_2')(d\langle R_z\rangle/dt)$. In view of the foregoing, we can obtain from (11) the equation

$$\frac{d\langle R_z\rangle}{dt} = \frac{\mu}{2T_1}\langle R_z\rangle^2 - \left(\frac{1}{T_1} + \frac{1}{T_2'(T)}\right)\langle R_z\rangle - \frac{\mu}{2T_1}N^2 + \left(\frac{1}{T_1} + \frac{1}{T_2'(T)}\right)N, \tag{17}$$

where it is taken into account that at the initial instant $t = 0$ the system was inverted, i.e., $\langle R_z\rangle_0 = N$, and $\langle R_{k0}{}^2\rangle_0 = 1/2N(N/2 + 1)$. The solution of (17) is

$$\langle R_z\rangle = \frac{T_1}{\mu}\left[\frac{1}{T_1} + \frac{1}{T_2'(T)} - \frac{1}{\tau_R}\,\mathrm{th}\,\frac{(t-t_0)}{2\tau_R}\right], \tag{18}$$

where $1/\tau_R = \mu N/T_1 - 1/T_1 - 1/T_2'(T)$, and t_0 is the instant when the superradiance reaches its maximum. Using the energy conservation law, we obtain the following expression for the intensity of the superradiance signal:

$$I_{\mathrm{SR}} = \frac{\hbar\omega_0\tau_0}{4\tau_R{}^2\mu}\,\mathrm{sech}^2\,\frac{(t-t_0)}{2\tau_R}. \tag{19}$$

We obtain thus the dependence of the Dicke superradiance pulse intensity on the decay time and on the parameters of the relaxation connected with the Orbach process.

We shall use (19) to analyze the temperature drops shown in Fig. 2. Since these drops were plotted for the superradiance maximum, i.e., when $t = t_0$, this analysis becomes much simpler (the hyperbolic secant turns out to be equal to unity) and in principle three experimental points on each drop suffice to obtain two unknown parameters of the pseudolocalized phonons: the activation energy ΔE and the phonon lifetime τ_{phn}. Since τ_R = 5–6 ns (Ref. 4) and τ_s = 3–5 ns, for a sample with pyrene-molecule density 0.1 mol.% we obtain (in the investigated temperature range)

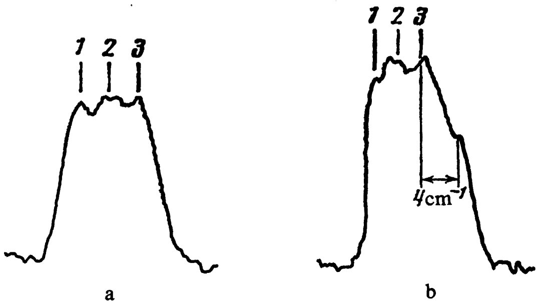

FIG. 3. Absorption spectra (spectra line of 0–0 transition) of pyrene in diphenyl at two values of the crystal temperature: a—1.5 K; b—4.2 K. 1—ν = 26744 cm^{-1}; 2—26739 cm^{-1}; 3—26735 cm^{-1}.

$\Delta E = 7 \pm 3\ \mathrm{cm}^{-1}$ and $\tau_{\mathrm{phn}} = 1$–5 ps. The spread of the obtained ΔE and τ_{phn}, just as in experiments on optical echo,[10–13] is due to the spreads of the parameters that enter in (19).

It should be noted that the influence of the dipole-dipole interaction of the impurity centers on the character of the relaxation begins to increase with increasing impurity density. This activates photon-excitation transport processes of the exciton type (see, e.g., Refs. 19 and 20). This question requires in principle a special analysis. Under the conditions of our experiment, however, such processes had low probability.

We note that inclusion, in the framework of the expounded calculation procedure (the nonequilibrium-statistical-operator method[17]), of only direct single-phonon relaxation processes described by the Hamiltonian (6) leads to the following expression for the spontaneous-decay time

$$T_1^{-1}(T) = \hbar^{-2} \sum_{k,\sigma} |g_{k,\sigma}|^2 R_{p_k}(T)\,\delta(p_k - l_k), \qquad (20)$$

where

$$R_{p_k}(T)$$

$$= \frac{2\pi}{\Omega_k} \exp[-D(2n_k+1)]\,J_{p_k}(2D(n_k(n_k+1))^{1/2}) \left(\frac{n_k+1}{n_k}\right)^{p_k/2},$$

$$D = \sum_{q,\alpha} |h_{jq\alpha}|^2 / (\hbar\Omega_q)^2;$$

here $\mathbf{J}_{p\,k}$ is a Bessel function of order p_k, $l_k = (\omega_k - \omega_0)/\Omega_k$; Ω_k is the effective phonon frequency corresponding to emission of photons with wave vector **k**, and n_k is the equilibrium average number of such phonons. Estimates based on the data of the present experiment point to a negligible change of T_1 in the temperature range 1.6–4.2 K. Thus, the description of the electron-phonon interaction by that part of the Hamiltonian of this interaction that is quadratic in the phonon operators is valid.

The assumption that transitions to vibrational levels become activated with increasing temperature (and conversely) with participation of localized phonons is confirmed by absorption spectra plotted at 1.6 and 4.2 K (Figs. 3a and 3b). It can be seen that at 1.6 K the absorption line of the 0–0 transition has the form of a trident. At a sample temperature 4.2 K the long-wave part acquires a "shelf" due to the appearance of pseudolocalized phonons and to activation of uncorrelated transitions of the impurity-molecule electrons on the vibrational sublevels, both near the lower (^1A_g) and near the upper ($^1B_{2u}$) levels. Raising the sample temperature will lead, furthermore, to shifts of each of the vibrational sublevels (1′ and 2′ in Fig. 1c), the shifts being in principle of unequal magnitude or sign. The appearance of the "shelf" in the absorption spectrum at 4.2 K is due to the 1′–2′ transition, whose frequency differs from that of the 0–0 transition by a value equal to the shifts of the sublevels 1′ and 2′ (i.e., by the energy width 4 cm^{-1} of the shelf).

CONCLUSION

We have thus investigated above, with a diphenyl crystal containing pyrene molecules as the example, the effect of phonons on the formation of Dicke superradiance, and have demonstrated the potential use of this phenomenon for the investigation of the relaxation parameters with their active participation. We have established that this relaxation is due to activation of the transitions of the pyrene molecules to vibrational sublevels with participation of pseudolocalized phonons. It follows from our study that Dicke superradiance can be produced under conditions of effective electron-phonon interaction, and this allows us in principle to expect superradiance not only on the 0–0 transition but also on the vibronic 2–4 transition. A correct analysis of this problem, however calls for solving the problem of optical superradiance of an "impurities + phonons + phonons" system, similar to that carried out, but under stringent limitations, in Refs. 21 and 22.

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